

TECHNICAL METHODS OF  
CHEMICAL ANALYSIS

**WORKS BY GEORGE LUNGE, Ph.D., Dr.Ing.**

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LONDON

GURNEY & JACKSON, 10 PATERNOSTER ROW



# TECHNICAL METHODS OF CHEMICAL ANALYSIS

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## ENGLISH TRANSLATION

FROM THE LATEST GERMAN EDITION, ADAPTED TO ENGLISH  
CONDITIONS OF MANUFACTURE

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VOLUME I.—PART II.

ERNST JERNEY AND JACKSON

... ERNOSTER ROW, LONDON

1908

## PART II

	PAGE
<b>Potassium Salts.</b>	
<i>Several Methods for the Determination of Potassium.</i>	
The potassium platinichloride method . . . . .	520
The perchloric acid method . . . . .	522
Other methods . . . . .	524
Modifications of the platinichloride method . . . . .	525
<i>Special Methods of Analysis</i> . . . . .	528
Stassfurt Salts . . . . .	528
A. Crude Salts — Carnalite, rock kieserite, kainite, sylvinite, "Hartsalz" . . . . .	528
Determination of potassium by the platinum method . . . . .	528
Determination by the perchloric acid method . . . . .	530
Determination of magnesium chloride, total magnesium, sulphuric acid . . . . .	531
Complete analysis of the crude salts . . . . .	531
B. Intermediate Products of Manufacture . . . . .	533
C. Manufactured Products . . . . .	533
1. Potassium chloride . . . . .	533
Determination of potassium by the platinum method . . . . .	533
By the perchloric acid method . . . . .	533
Determination of:—	
Sodium chloride . . . . .	534
Magnesium salts, water, insoluble matter . . . . .	535
2. Potassium sulphate . . . . .	535
General considerations . . . . .	535
Determination of:—	
Sulphate . . . . .	536
Potassium by the platinum method . . . . .	536
By the perchloric acid method . . . . .	537
3. Potassium salt manures . . . . .	537
Nitre . . . . .	538
A. Raw Materials . . . . .	538
1. Chili saltpetre . . . . .	538
2. Potassium chloride . . . . .	538

B. Intermediate Products . . . . .	530
C. Final Product—Nitre . . . . .	539
Determination of:—	
Moisture, chlorine, insoluble impurities, perchlorate, potassium, chlorate, iodine . . . . .	539
III. Potassium Carbonate . . . . .	540
A. Raw Materials . . . . .	540
1. Potassium chloride . . . . .	540
2. Beet ashes . . . . .	540
B. Intermediate Products . . . . .	543
Carbonated liquors . . . . .	543
C. Final Products and By-products . . . . .	543
1. Potassium carbonate . . . . .	543
2. Impure potassium carbonate, molasses carbonate, and beet ash carbonate . . . . .	545
3. Hydrated potassium carbonate . . . . .	545
<b>Cyanogen Compounds.</b>	
I. <i>Simple Cyanides</i> . . . . .	546
1. Gravimetric methods of analysis . . . . .	546
2. Volumetric methods of analysis:—	
Liebig's method . . . . .	547
Fordos and Gélis' method . . . . .	547
Hydrocyanic acid . . . . .	548
Cherry laurel and bitter almond waters . . . . .	548
Potassium cyanide . . . . .	549
Estimation of cyanogen by Liebig's method . . . . .	550
The Fordos and Gélis method for the estimation of cyanogen . . . . .	554
Sodium cyanide . . . . .	554
Ammonium cyanide . . . . .	554
Cyanides of the alkaline earths . . . . .	555
Mercuric cyanide . . . . .	555
II. <i>Double Cyanides</i> . . . . .	555
1. Potassium ferrocyanide, yellow prussiate of potash . . . . .	555
Examination of "spont-oxide" . . . . .	555
Determination of:—	
Moisture . . . . .	
Prussian blue . . . . .	
Knublauch's method . . . . .	

# CONTENTS

	PAGE		PAGE
II. <i>Double Cyanides—Continued.</i>		<i>Physical Examination—Continued.</i>	
Zulkowsky's method . . . . .	558	2. Specific gravity . . . . .	590
Nauss' method . . . . .	558	3. Specific porosity, or water-absorption . . . . .	591
Möldenhauer and Leybold's method . . . . .	560	4. Permeability to water . . . . .	591
Drehschmidt's method . . . . .	560	II. Structure and Hardness :—	
Intermediate products of manufacture ;		1. Structure of the material . . . . .	592
calcium ferrocyanide . . . . .	561	2. Flaws in the glaze . . . . .	592
Commercial products . . . . .	562	3. Hardness . . . . .	593
Potassium ferrocyanide . . . . .	562	III. Resistance to Wear :—	
Potassium ferricyanide . . . . .	563	1. Resistance to friction . . . . .	593
Sodium ferrocyanide . . . . .	563	2. Toughness . . . . .	594
2. Other cyanogen double salts . . . . .	563	IV. Durability :—	
III. <i>Thiocyanates</i> . . . . .	564	1. Resistance to pressure . . . . .	594
Ammonium thiocyanate . . . . .	564	2. Testing pipes for external pressure . . . . .	595
Potassium thiocyanate . . . . .	567	3. Testing pipes for internal pressure . . . . .	595
Literature . . . . .	567	4. The breaking strength of roofing tiles, etc. . . . .	595
Clay.		V. Durability towards Weathering :—	
General properties . . . . .	568	1. Examination for detrimental en-	
<i>Physical Examination</i> . . . . .	569	closures . . . . .	595
I. Mineral Mixtures and their State of		2. Permanence towards frost . . . . .	596
Division . . . . .	569	VI. "Fire-resisting" Qualities . . . . .	597
II. Plasticity . . . . .	571	<i>Chemical Analysis</i> . . . . .	598
III. Behaviour of Clays on Drying . . . . .	572	I. General Analysis :—	
IV. Behaviour of Clays on Firing . . . . .	573	1. Determination of the composition of	
Evenness of colour . . . . .	572	fired articles . . . . .	598
Colour . . . . .	574	2. Examination for lead . . . . .	599
Density . . . . .	575	3. Estimation of alumina . . . . .	600
Vitrification . . . . .	575	II. Estimation of Soluble Salts . . . . .	600
Firing contraction . . . . .	576	III. Stability towards Acids . . . . .	601
Refractoriness . . . . .	576	IV. Stability of Glazes towards Weather-	
Methods of determination :—		ing . . . . .	602
Bischof's method . . . . .	577	<i>The Examination of Roofing Slates</i> . . . . .	602
Seger cones . . . . .	577	Imbibition test . . . . .	603
Kreiling's method . . . . .	578	Weathering test . . . . .	603
<i>Chemical Analysis</i> . . . . .	580	Chemical Analysis . . . . .	603
I. Total or Centesimal Analysis . . . . .	580	Literature . . . . .	604
1. Fusion with alkali carbonate . . . . .	580		
Determination of :—		Aluminium Salts and Alumina.	
Silica, titanio acid . . . . .	581	<i>Raw Materials :—</i>	
Alumina, oxide of iron . . . . .	582	Kaolin . . . . .	605
Manganese, calcium, magnesium . . . . .	583	Bauxite . . . . .	605
2. Treatment with hydrofluoric acid . . . . .	583	<i>Control of Working Conditions :—</i>	
3. Estimation of other constituents :—		Residue . . . . .	607
Sulphuric acid, pyrites, carbon,		Aluminate solution . . . . .	607
dioxide, loss on ignition . . . . .	584	Filter-press cakes . . . . .	608
II. Rational Analysis . . . . .	585	<i>Finished Products</i> . . . . .	608
Lunge and Millberg's method . . . . .	585	I. Aluminium Sulphate . . . . .	608
Kreiling's method . . . . .	586	Qualitative examination . . . . .	608
Other methods . . . . .	587	Quantitative analysis . . . . .	610
Literature . . . . .	588	Determination of :—	
Clay Wares used for Building Purposes ;		Alumina . . . . .	610
Earthenware and Glazes.		Iron . . . . .	614
<i>Physical Examination</i> . . . . .	589	Free acid . . . . .	615
I. Density :—		Other constituents . . . . .	617
1. Specific volume . . . . .	590		

# CONTENTS

	PAGE
<i>Finished Products—Continued.</i>	
II. Potassium, Sodium and Ammonium Alums . . . . .	617
III. Sodium Aluminate . . . . .	617
IV. Alumina . . . . .	619
V. Aluminium Salts used in Dyeing, etc. (Acetate, Thiocyanate, etc.) . . . . .	620
Literature . . . . .	620

## Glass.

I. Raw Materials . . . . .	621
1. Silica and silicates . . . . .	621
Sand . . . . .	622
Quartz . . . . .	623
Flint . . . . .	623
Natural silicates . . . . .	623
2. Boric acid and borates . . . . .	624
Boric acid . . . . .	624
Borax . . . . .	625
Natural borates . . . . .	625
3. Alkaline fluxes . . . . .	627
Potassium carbonate . . . . .	627
Sodium carbonate . . . . .	627
Sodium sulphate . . . . .	627
4. Lime . . . . .	628
5. Lead oxide . . . . .	628
6. Other oxides and fluxes . . . . .	629
Zinc oxide and baryta . . . . .	629
Fluor-spar . . . . .	629
Cullet . . . . .	630
7. Decolorising agents . . . . .	630
Manganese dioxide . . . . .	630
Nickel oxide, selenium and selenium compounds, arsenious oxide and nitre, compressed oxygen . . . . .	631
8. Colouring agents . . . . .	631
Iron compounds . . . . .	631
Compounds of manganese, copper, cobalt, chromium, nickel, uranium, antimony . . . . .	632
Silver, gold, selenium, cadmium . . . . .	633
Organic substances . . . . .	633
Substances which produce opacity:—	
Tin oxide, arsenic, bone ash, guano, cryolite, cryolite substitutes . . . . .	633
Fluor-spar . . . . .	634

II. The Composition and Testing of Glass . . . . .	634
1. The Composition of Glass . . . . .	634
Alkali-lime glass . . . . .	634
Alumina-lime glass . . . . .	635
Boro-silicate glass . . . . .	635
Lead glass . . . . .	635
II. The Testing of Glass for Resistance against the Action of the Weather, Water, and Chemical Agents . . . . .	635
Influence of the composition of the glass . . . . .	635

II. The Testing of Glass, etc.—Continued.	PAGE
Action of acids, alkalis, and other chemical agents . . . . .	636
Methods of testing, and results . . . . .	638

## III. The Analysis of Glass . . . . .

Qualitative Examination . . . . .	641
Examination for all constituents except silica, boric acid, and fluorine . . . . .	641
Silica, boric acid, and fluorine . . . . .	642
Quantitative Analysis . . . . .	644
Preparation of the substance for analysis . . . . .	644
Decomposition . . . . .	644
1. Leadless alkali-lime and alumina-lime glass . . . . .	644
Fusion with sodium carbonate . . . . .	644
Decomposition with hydrofluoric acid . . . . .	647
Decomposition with calcium carbonate and ammonium chloride . . . . .	649
2. Lead glass . . . . .	650
Semi-crystal glass . . . . .	650
Flint glass . . . . .	651
3. Glass containing boric acid . . . . .	652
4. Glass containing fluorine . . . . .	653
5. Glass containing phosphoric acid . . . . .	654
6. Coloured glass . . . . .	655
7. Glass enamels, metallic enamels, and enamel colours . . . . .	656
Literature . . . . .	657

## Calcareous Cements.

Raw Materials . . . . .	658
I. Lime . . . . .	658
A. Limestone . . . . .	658
1. Preliminary tests, gas-volumetric determination of the calcium carbonate . . . . .	659
The Scheibler-Dietrich apparatus . . . . .	659
The Baur-Cramer apparatus . . . . .	660
Volumetric determination of the calcium oxide or carbonate . . . . .	663
Determination of magnesium oxide . . . . .	663
Clay . . . . .	664
2. Complete analysis . . . . .	665
Determination of:—	
Moisture . . . . .	665
Loss on ignition, carbon dioxide, undecomposed matter (clay and sand), silica, alumina, and ferric oxide . . . . .	666
Calcium . . . . .	667
Magnesium, sulphuric acid . . . . .	668
B. Quicklime . . . . .	669
1. Keeping properties . . . . .	669

# CONTENTS

	PAGE		PAGE
B. <i>Quicklime—Continued.</i>		B. <i>Artificial Hydraulic Cements, Portland Cement, etc.—Continued.</i>	
2. Slaking power . . . . .	669	Specifications for Portland cement .	695
3. Increase of volume on slaking .	670	Clinker . . . . .	697
Michaëlis volumenometer . . . . .	670	Ash and slurry . . . . .	697
C. <i>Lime</i> . . . . .	671	Examination of the physical properties of Portland cement—	
Tensile strength test . . . . .	671	Specific gravity . . . . .	698
Determination of lime in mortar .	672	Degree of fineness of cement and sand . . . . .	701
Frühling's method . . . . .	672	The flourimeter . . . . .	703
Holmblad's method . . . . .	673	Hydraulicity . . . . .	704
II. <i>Hydraulic Admixtures</i> . . . . .	674	Time of setting . . . . .	706
A. <i>Natural Pozzuolanas: Pozzuolana proper, Santorin Earth, and Trass</i>	674	Tests for permanency of volume .	706
Composition . . . . .	675	Accelerated tests for permanency of volume:—	
1. Determination of hygroscopic water and of water of hydration; loss on ignition . . . . .	676	Heintzel's calcining test . . . . .	709
2. Degree of fineness . . . . .	677	Roasting test . . . . .	709
3. Needle test . . . . .	677	Boiling test . . . . .	710
4. Tensile and crushing strength .	678	Tetmajer's investigations on the tests for permanency of volume .	710
B. <i>Artificial Pozzuolanas</i> . . . . .	679	Increase of volume on mixing with sand . . . . .	710
Blast-furnace slag . . . . .	679	Permeability to water . . . . .	711
Composition . . . . .	679	Resistance to frost . . . . .	713
Strength . . . . .	680	Abrasion test . . . . .	714
III. <i>Hydraulic Cements</i> . . . . .	680	Mechanical tests for Portland cement	714
A. <i>Natural Hydraulic Cements</i> . . . . .	680	The preparation of the test pieces .	715
1. <i>Hydraulic Lime</i> . . . . .	681	The sand test . . . . .	718
Analysis . . . . .	681	The tensile strain . . . . .	721
Determination of:—		The crushing strain . . . . .	724
Silica and gangue . . . . .	681	The adhesion . . . . .	725
Alumina and ferric oxides . .	682	The bending strain . . . . .	726
Calcium and magnesium, iron, sulphuric acid, bitumen . . . . .	683	Adulterations of Portland cement .	727
The examination of marls . . . . .	683	IV. <i>Gypsum</i> . . . . .	729
Differentiation of hydraulic lime and Roman cement . . . . .	684	Literature . . . . .	731
Permanency of volume . . . . .	684	Drinking Water and Water Supplies.	
2. <i>Roman cement</i> . . . . .	685	Rain water, well water . . . . .	732
3. <i>Dolomitic or magnesium cement</i> .	687	Spring water, river water . . . . .	733
B. <i>Artificial Hydraulic Cements, Portland Cement, etc.</i> . . . . .	688	Impurities in natural waters . . . . .	733
Raw Materials:—		Sampling . . . . .	733
Clay . . . . .	688	Physical Examination of Water	
Estimation of the sand in clay, elutriation . . . . .	689	Determination of temperature .	734
Nobel's apparatus . . . . .	690	Clearness, colour, smell and taste .	734
Schöne's apparatus . . . . .	690	Chemical Examination of Water	
Portland cement . . . . .	691	Statement of results . . . . .	736
Chemical analysis . . . . .	692	Residue on evaporation . . . . .	736
Determination of:—		Alkalinity . . . . .	737
Silica, sesquioxides . . . . .	692	Acidity . . . . .	738
Calcium oxide, magnesium oxide, sulphuric acid, sulphur . . . . .	693	Hardness . . . . .	739
Alkalis . . . . .	694	Clark's soap test . . . . .	740
The composition of Portland cement . . . . .		Reducing power, or "oxygen absorption" . . . . .	742
		Silica, sulphuric acid . . . . .	748
		Chlorine . . . . .	

	PAGE
<i>Chemical Examination of Water—Continued.</i>	
Nitric acid . . . . .	751
The Schulze-Tiemann method of determination . . . . .	753
Ulsch's method . . . . .	753
Reduction by the zinc-copper couple . . . . .	753
The Marx-Trommsdorf method . . . . .	754
Colorimetric determination with brucine . . . . .	756
Colorimetric determination with phenolsulphonic acid . . . . .	758
Nitrous acid . . . . .	759
Phosphoric acid, carbonic acid . . . . .	762
Calcium and magnesium . . . . .	764
Sodium and potassium . . . . .	764
Ammonia . . . . .	765
Nessler's reagent . . . . .	766
Albuminoid ammonia . . . . .	769
Proteid ammonia . . . . .	770
Iron . . . . .	772
Colorimetric estimation . . . . .	773
Lead . . . . .	775
The determination of dissolved gases . . . . .	776
Nitrogen, oxygen, methane . . . . .	777
Adeney's apparatus for the extraction and analysis of the gases dissolved in water . . . . .	780
Winkler's iodometric method of analysis . . . . .	782
"Rate of decay" of water . . . . .	785
Solubility of oxygen and nitrogen in water . . . . .	785
Hydrogen sulphide . . . . .	786
<i>Microscopic Examination</i> . . . . .	789
<i>Bacteriological Examination</i> . . . . .	789
Preparation of nutrient gelatine . . . . .	790
Counting the bacteria . . . . .	791
<i>Interpretation of Results</i> . . . . .	793
Literature . . . . .	797
 <b>Feed Water for Boilers and Water for other Technical Purposes.</b>	
Hardness . . . . .	799
Alkalinity . . . . .	800
Total alkaline earths . . . . .	800
Sulphates, magnesium, iron, silica . . . . .	801
Chlorides . . . . .	802
Acid waters . . . . .	802
Special tests to determine the amounts of lime and of sodium carbonate necessary for the treatment of water . . . . .	802
Pfeifer and Wartha's method . . . . .	804
Determination of the magnesium . . . . .	804
Blacher's method . . . . .	805
Literature . . . . .	806

	PAGE
<b>Sewage and Effluents.</b>	
Constituents of effluents . . . . .	807
Sampling . . . . .	811
<i>Chemical Examination</i>	
A. Preliminary Examination on the spot . . . . .	811
B. Examination in the Laboratory	
1. Residue on evaporation and loss on ignition . . . . .	812
2. Suspended and dissolved organic matter and inorganic matter . . . . .	813
3. The determination of colloidal matter . . . . .	814
4. Oxidisability or oxygen-consuming power . . . . .	815
5. Alkalinity . . . . .	816
6. Free Acids . . . . .	817
7. Nitrogen	
A. Total nitrogen, the Kjeldahl-Jodlbaur method . . . . .	817
B. Ammonia . . . . .	818
C. Nitrous acid . . . . .	820
D. Nitric acid . . . . .	821
The zinc-iron method . . . . .	821
The Schulze-Tiemann modification of the Schloßing method . . . . .	822
E. Suspended and dissolved organic nitrogen and ammonia . . . . .	824
F. Combined organic nitrogen (albuminoid ammonia) . . . . .	824
8. Sulphuretted hydrogen and sulphides . . . . .	825
9. Chlorine . . . . .	825
10. Other mineral substances . . . . .	826
11. Albuminoid compounds, sugar, starch, and yeast . . . . .	826
12. Oxygen . . . . .	827
Müller's "Tenax" apparatus . . . . .	827
13. Organic carbon . . . . .	829
A. Organic carbon in the filtered water . . . . .	830
B. Organic carbon in the suspended matter . . . . .	831
14. Carbonic acid . . . . .	832
15. Detection of excreta . . . . .	832
16. Detection of coal-gas products . . . . .	833
17. Tests for putrescibility; fermentation experiments on effluents . . . . .	833
<i>Microscopic and Bacteriological Examination</i>	
Criteria as to the Contamination due to Effluents and their Injurious Effects . . . . .	835
1. Effects on fish-culture . . . . .	835
A. By examination of the fauna and flora of the contaminated water . . . . .	835
B. By examination of the water and by experiments on its injurious effect on fish . . . . .	836
2. Injurious effect on live stock . . . . .	837

# CONTENTS

	PAGE		PAGE
<i>Criteria as to the Contamination Due to Effluents, etc.—Continued.</i>		I. <i>Estimation of the Natural Constituents of Air—Continued.</i>	
3. Injurious effect for industrial purposes	838	Gas-volumetric methods, Haldane's method	873
4. Injurious effect on the soil	839	Approximate methods, Lunge and Zeckendorf's method	875
5. Injurious effect on plants	839	Wolpert's method	876
6. Injurious action on ground and well waters	840	4. Aqueous vapour	877
Literature	840	5. Hydrogen peroxide	879
		6. Ozone	881
<b>Soils.</b>		7. Ammonia	882
Classification of soils	841	8. Nitrous (and nitric) acid	882
General considerations regarding the examination of soils	842	II. <i>Estimation of the Impurities in the Air of Towns and of Confined Spaces.</i>	883
I. <i>Sampling</i>	843	Methods of sampling	883
II. <i>Mechanical Examination</i>	844	1. Sulphurous acid	884
III. <i>Physical Examination</i>	849	2. Hydrogen sulphide	888
Determination of:—		3. Hydrochloric acid	888
Capillary attraction	849	4. Carbon monoxide	889
Capacity for water	849	The palladious chloride test	889
Absorptive power for salts in solution	849	The spectroscopic test	890
Evolution of heat on moistening	851	Haldane's colorimetric test	892
IV. <i>Chemical Examination</i>	851	Colorimetric test after the addition of reagents	893
Treatment with:—		The flame-cap test	894
Hot concentrated hydrochloric acid	852	The quantitative determination of carbon monoxide	894
Citric acid	852	5. Hydrocarbons:—	
Water containing carbonic acid	853	Methane, acetylene	897
Concentrated hydrochloric acid	854	Benzene, petroleum vapour	898
Concentrated sulphuric acid	855	6. Organic matter	898
Hydrofluoric acid	856	7. Soot and smoke	899
<i>The Determination of the Individual Constituents of Soil:—</i>		8. Dust	901
Hygroscopic water, chemically combined water, or loss on ignition, humus	857	III. <i>The Estimation in Air of Impurities associated with Specific Industries</i>	903
Carbon dioxide	859	1. Chlorine, bromine, and iodine; 2. Phosphorous trichloride	903
Total nitrogen, ammoniacal nitrogen, nitric-nitrogen	861	3. Hydrofluoric acid; 4. Cyanogen and hydrocyanic acid; 5. Hydrogen phosphide; 6. Hydrogen arsenide	904
Organic nitrogen, chlorine, sulphur	862	7. Mercury vapour; 8. Carbon bisulphide	905
Ferrous iron, copper, and lead	864	9. Ether vapour; 10. Mercaptan	906
Zinc	865	II. Aniline	907
Literature	865	<i>Effects of the Impurities in Air</i>	909
		<i>Tobacco Smoke</i>	910
<b>Air.</b>		Literature	911
The constituents of air	866	APPENDIX	913
I. <i>Estimation of the Normal Constituents of Air</i>	867	INDEX	977
1. Oxygen	867		
2. Nitrogen	869		
3. Carbon dioxide	869		
Pettenkofer's method	870		

SPECIAL METHODS OF TECHNICAL  
ANALYSIS—*Continued*



## POTASSIUM SALTS

By Dr L. TIETJENS, Leopoldshall

### GENERAL METHODS FOR THE DETERMINATION OF POTASSIUM

OF the methods used for the determination of potassium, that of Fresenius, in which the potassium is separated as potassium platinichloride, is the most important, and has found general acceptance in the potassium salt industry. Amongst other methods, the determination of potassium as perchlorate, which has been very thoroughly worked out by Wense<sup>1</sup> and by Caspari,<sup>2</sup> may be regarded as of equal value with the older platinum method, a statement substantiated by the fact that the International Congress for Applied Chemistry (1903) decided to class it as an international method of determination, together with the Fresenius method.

**A. The Potassium platinichloride method.**—In the separation of potassium as potassium platinichloride by Fresenius' shortened method, which has been thoroughly worked out by Brecht,<sup>3</sup> the use of pure platinic chloride solution is of the utmost importance. It must be free from platinous chloride and oxides of nitrogen, and contain at most only a small quantity of free hydrochloric acid. Precautions must also be taken to guard against the introduction of other impurities, such as sulphuric acid from impure reagents, and potassium platinichloride from the incomplete washing of recovered platinum from platinum residues. The preparation of the platinic chloride solution is described below.

For the washing of the potassium platinichloride precipitate, absolute alcohol should invariably be used, because, firstly, whilst potassium platinichloride is soluble only to the extent of 1 : 40,000 in absolute alcohol, in 80 per cent. alcohol the solubility increases to 1 : 25,000; and secondly, the double salts of platinic chloride with sodium, calcium, and magnesium met with in course of analysis, are at least just as soluble (the sodium salt is decidedly more soluble) in absolute than

<sup>1</sup> *Z. angew. Chem.*, 1891, 4, 691.

<sup>2</sup> *Ibid.*, 1893, 6, 68; cf. also, Kreider, *Z. anorg. Chem.*, 1895, 9, 343.

<sup>3</sup> *Z. anal. Chem.*, 1879, 18, 509.

in more dilute alcohol. The observations recorded, that more correct results are obtained by the use of 80 per cent. alcohol than with the more absolute, must be traced to a compensation of errors, due to a high value being obtained for the potassium platinichloride caused through impurities in the platinic chloride, being compensated by the greater solubility of potassium platinichloride in 80 per cent. alcohol. The proposal made by the "Verband landw. Versuchsstationen im Deutschen Reiche" with regard to the removal of the impurities in the potassium platinichloride precipitate, viz., by dissolving in hot water and filtering off the impurities, can only partially effect the desired end, because the precipitate may contain in addition to platinous chloride and insoluble sulphates, barium chloride, arising from the use of an excess in the precipitation of sulphuric acid and potassium platinichloride introduced by the use of an impure platinic chloride solution. These impurities are naturally not removed from the dissolved precipitate by treatment with hot water. Provided a definite, measured quantity of platinic chloride solution is always added, it is simpler to evaporate about 10 c.c. of the platinic chloride solution to dryness, to take up and wash the residue with alcohol, and to weigh it; the impurities in the reagent are thus determined, and a proportional weight is then deducted from the weight of potassium platinichloride found.

For the collection of the potassium platinichloride precipitate, either a filter paper or a Gooch crucible is employed. In the Stassfurt works filter paper is invariably used, and preference is given to a Swedish paper<sup>1</sup> which permits of quick filtration and is at the same time sufficiently retentive. Filtration is generally hastened by suction. When frequent daily determinations of potassium have to be carried out, the washing of the precipitates may with advantage be done by means of a 10 litre jar placed about 60 cm. above the bench and fitted with a cork, glass tube and rubber tubing, to which a pinchcock and gas jet are attached, instead of by means of an ordinary wash-bottle.

For the preparation of platinic chloride, waste alcoholic washings and potassium platinichloride precipitates from previous analyses are generally used. The alcoholic washings are diluted with one-third of their volume of water, and after addition of sodium carbonate heated to boiling on the water-bath in a large porcelain dish, and the potassium platinichloride to be reduced gradually stirred in. The heating and the addition of sodium carbonate must be continued until the liquid above the reduced platinum is perfectly clear, alkaline, and of a faint yellow colour. The solution is then decanted off and the reduced platinum purified by boiling with hydrochloric acid and then with water, evaporating to dryness on the water-bath, and any organic platinum compounds present decomposed by careful ignition. After ignition, the finely

ground platinum is boiled once with concentrated nitric acid, the liquid decanted off, and the platinum dissolved in a large porcelain dish on the water-bath by the gradual addition of about four times its weight of warm hydrochloric and nitric acids, in the proportion of four parts of hydrochloric acid to one part of nitric. When the solution is completed, the liquid is evaporated till a drop taken out on a glass rod solidifies. After cooling, the crystalline mass of platinic chloride is taken up with water, the solution filtered and diluted so that 10 c.c. contain 1 g. of platinum (sp. gr. 1.18). Should the solution be contaminated by platinous chloride or nitric oxide compounds, the former is converted into platinic chloride by heating with fuming hydrochloric acid and a small quantity of nitric acid, whilst the latter are removed by alternate evaporations with hydrochloric acid and water.

Platinum residues, either washings or precipitates, may also be reduced by zinc dust.

Should scrap platinum be used for the preparation of the chloride, the possible presence of iridium necessitates the addition of ammonium chloride to precipitate the platinum and subsequent reduction. The purity of the platinic chloride solution is best checked against an "80 per cent. potassium chloride" prepared from chemically pure substances of known composition.

**B. The Perchloric acid method.**—This method possesses the great advantage over the determination as potassium platinichloride in being more suitable for the analysis of sulphates, and is coming more and more into use in the Stassfurt works. The perchlorates of sodium, calcium, and magnesium, as well as that of barium, are soluble in alcohol, so that a slight excess of barium chloride used for the precipitation of the sulphates is not disadvantageous. In the platinum method, on the contrary, any excess of barium chloride must be avoided, because barium platinichloride is decomposed by alcohol. According to Precht,<sup>1</sup> the extent of this decomposition is given by the following figures:—

1 gram-molecule BaCl <sub>2</sub> evaporated with the following amounts of PtCl <sub>4</sub> :	Percentages of the BaCl <sub>2</sub> present which separate as insoluble:
1 gram-molecule	68.0
1.3 "	61.3
1.5 "	53.4
1.8 "	42.0
2.0 "	29.8
2.5 "	16.1
3.0 "	5.2
4.0 "	3.0

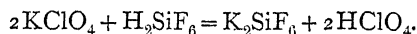
Potassium perchlorate being of a granular nature, permits of easy filtration and washing; further, the evaporation of the precipitates may

<sup>1</sup> *Z. anal. Chem.*, 1879, 18, 516.

be carried further than in the platinum method without disadvantage, and is in fact desirable, so as to effect the complete decomposition of the chlorides into perchlorates. The perchloric acid method is also more economical than the platinum method, and does not give rise to those injurious effects which at times occur in working up platinum residues.

For the preparation of perchloric acid, potassium perchlorate or chlorate is employed. The former always occurs as an impurity in Chili saltpetre, and is prepared largely from this source. Perchloric acid is prepared according to Caspari<sup>1</sup> as follows:—

Potassium chlorate is heated in a Hessian crucible, 15 cm. high, in a brick furnace until the molten mass thickens to a pasty condition showing the end of the decomposition to perchlorate. The ground-up melt is then boiled with one and a half times its weight of water, the potassium chloride solution poured off when cold, the residue washed with cold water to complete the removal of the potassium chloride, and dried. The potassium perchlorate is then converted into perchloric acid by decomposition with hydrofluosilicic acid, according to the equation:—



The potassium perchlorate is dissolved in about seven times its weight of hot water in a large porcelain dish, and a slight excess of hydrofluosilicic acid stirred in. The boiling is continued until all small, hard lumps of potassium perchlorate have disappeared, the evaporated water being made up by fresh additions. After cooling, the gelatinous potassium hydrofluosilicate is filtered or decanted off, and the solution concentrated as far as possible on the water-bath; after standing in a cold place for twenty-four hours, any potassium hydrofluosilicate remaining in solution along with a small quantity of potassium perchlorate separates out. The solution is then filtered through an asbestos filter, diluted with an equal volume of water, and any remaining hydrofluosilicic acid and sulphuric acid, which may be present as an impurity from the hydrofluosilicic acid, precipitated with barium chloride. When the solution has cleared, it is evaporated till all hydrochloric acid fumes are driven off and white fumes of perchloric acid appear. On cooling, a further portion of potassium perchlorate and needles of sodium perchlorate separate out, from which the free concentrated acid is filtered off. The filtrate is finally diluted with an equal volume of water and allowed to stand for from one to two days, during which time any remaining barium hydrofluosilicate and barium sulphate separate out. After further filtration the reagent is ready for use.

Kreider<sup>2</sup> gives the following method for the preparation of perchloric acid:—

One hundred to three hundred g. of sodium chlorate are heated in a

<sup>1</sup> *loc. cit.*

<sup>2</sup> *Loc. cit.*

glass retort until the evolution of oxygen begins. After about one to two hours the molten mass becomes solid, showing that the decomposition of chlorate into perchlorate and chloride is complete. After cooling, the mass is washed out into a large porcelain dish, and treated with sufficient hydrochloric acid, to decompose any remaining chlorate. The whole contents of the dish are then evaporated to dryness, either on the water-bath or over a free flame, being continually stirred during the evaporation. The broken-up residue is then treated with an excess of the strongest possible hydrochloric acid; perchloric acid and sodium chloride are formed, which are separated by filtration through a Gooch crucible. The filtrate is evaporated on the water-bath until all the hydrochloric acid is removed and white fumes of perchloric acid commence to come off.

**C. Other Methods for the determination of Potassium.**—The separation of potassium as *potassium hydrogen tartrate*, for a long time in vogue at Stassfurt, has been much improved by Frank,<sup>1</sup> Fleischer,<sup>2</sup> and especially by Bayer.<sup>3</sup> To the solution containing potassium, Bayer adds sodium carbonate equivalent to the amount of acids present, and then acetic and tartaric acids in excess. Absolute alcohol is then added to the heated solution until this latter contains 25 per cent. of alcohol. After standing for two hours, the cleared solution is filtered off, the precipitate freed from sodium bitartrate by washing with 25 per cent. alcohol, and finally washed with 50 per cent. alcohol. The precipitate along with the filter paper are then titrated with  $N/10$  sodium hydroxide, using phenolphthalein as indicator.

The *alum method*,<sup>4</sup> which was also used for many years at Stassfurt, consists in evaporating the solution of the potassium salt with alum mother liquor until a surface separation of the potassium salt occurs; the solution is then allowed to crystallise out, and the separated salt washed, first with the mother liquor, then with water, dried, weighed, and calculated to potassium chloride.

Rose<sup>5</sup> has proposed the separation of potassium as *potassium silicofluoride*, by treating the concentrated solution of the potassium salt with an excess of pure hydrofluosilicic acid and an equal volume of alcohol. The gelatinous precipitate of potassium fluosilicate is collected on a weighed filter paper, washed with 50 per cent. alcohol, dried at 100°, and weighed.

The following methods have also been suggested:—The precipitation of the potassium as *potassium picrate*, proposed by Hager,<sup>6</sup> as *potassium bismuth thiosulphite* by Carnot<sup>7</sup> and Campari,<sup>8</sup> and Gay-

<sup>1</sup> *Dingl. polyt. J.*, 1867, 183, 40.

<sup>2</sup> *Z. anal. Chem.*, 1870, 9, 331.

<sup>3</sup> *Chem. Zeit.*, 1893, 17, 686.

<sup>4</sup> *Berg. u. Hüttenm. Zeit.*, 1866, 273.

<sup>5</sup> *J. prakt. Chem.*, 1867, 102, 7.

<sup>6</sup> *Pharm. Centr.*, 22, 225.

<sup>7</sup> *Comptes rend.*, 1878, 86, 478.

<sup>8</sup> *Z. anal. Chem.*, 1884, 23, 60.

Lussac's method of determining potassium chloride by the reduction in temperature produced on dissolving potassium chloride and sodium chloride in water.

The following *modifications of the platinum method* have also been proposed:—

Vogel and Häfcke<sup>1</sup> evade the precipitation of sulphuric acid (in potassium salts containing sulphates) by treating the sulphates of the alkalis with a slight excess of platinic chloride, a method previously suggested by Finkener. For the analysis of kainite, for instance, 10 g. of the salt are dissolved in 300 c.c. of water in a 500 c.c. flask, boiled and, after cooling the contents, made up to the 500 c.c. mark. Fifty c.c. (1 g.) of the solution are evaporated to dryness in a platinum dish, and after cooling 20 c.c. of a solution of neutral ammonium carbonate (Schaffgotsch's solution) added in order to precipitate calcium and magnesium. The bulky precipitate first formed goes into solution on vigorous stirring, a crystalline precipitate separating later. The separation of the calcium and magnesium requires about twelve hours. The precipitate is then removed to a small filter paper and washed with 10 to 15 c.c. of Schaffgotsch's solution. The filtrate, after addition of a few drops of concentrated sulphuric acid, is evaporated to dryness in a platinum dish, the dish being covered with a clock-glass to prevent spitting of the contents, due to liberation of carbon dioxide. The residue is then gently ignited to remove ammonium salts, dissolved in hot water, filtered through a small filter paper into a porcelain dish about 10 cm. in diameter, platinic chloride and some hydrochloric acid added, and the whole evaporated to a syrupy consistency. The residue, a cold crystalline mass is rubbed up finely with 20 to 25 c.c. of a mixture of 2 parts of absolute alcohol and 1 part of ether, filtered through a Gooch crucible, and washed until the washings are colourless. The residue remaining in the crucible, consisting of potassium platinic chloride and sodium sulphate, after being dried for five to ten minutes in a drying oven, is decomposed in a current of hydrogen, the crucible being fitted up like a Rose crucible, care being taken that the temperature does not rise much above 250°. As a rule, the reduction is complete in from ten to fifteen minutes. The reduced platinum is washed in the same crucible with hot water. The crucible is then dried, ignited, weighed, and the content of potassium calculated.

Whilst from a theoretical standpoint nothing can be said against this method, it is not so favoured by technical chemists as the older shortened platinum or perchloric acid methods, on account of the more lengthy and complicated manipulation involved. The long time necessary (twelve hours) for the precipitation of the calcium and magnesium also renders the method unsuitable, when, as in the majority of cases, resu-

<sup>1</sup> Landw. Versuchsst., xi., vii., 97.

are demanded at short notice. It finds its most useful application in the determination of potassium in organic substances. An advantage of the method lies in the small amounts of platinic chloride and of alcohol used.

Hilgard<sup>1</sup> avoids the direct weighing of the potassium platinichloride and recommends weighing the reduced platinum. For this purpose he uses a small platinum crucible, the lower half of the inside of which is covered with spongy platinum, prepared by decomposing a few decigrams of potassium platinichloride in the crucible, which is inclined and turned during the heating. This layer of spongy platinum renders the reduction of potassium platinichloride possible at a comparatively low temperature. When the reduction is completed, most of the potassium chloride is driven off by prolonged, strong ignition. Complete decomposition is recognised by adding a few drops of concentrated hydrochloric acid to the cold contents of the crucible, and warming; if a yellow coloration is observed, the ignition is repeated after the addition of some oxalic acid. The spongy platinum is then thoroughly washed by decantation, ignited, and weighed.

Similarly, in order to avoid weighing the potassium platinichloride the decomposition of the double salt may be carried out by reducing substances such as formic or oxalic acids, magnesium or zinc dust, and either the separated platinum determined or the chlorine titrated in the filtrate. Of the latter methods, that of Fabre<sup>2</sup> simplified by Diamant<sup>3</sup> is the most favourable. Fabre reduces the dissolved potassium platinichloride with magnesium powder in warm solution, filters off the platinum and the excess of magnesium powder, and estimates the chlorine in the filtrate volumetrically. Diamant used zinc dust; the reduction then takes place in the cold. This obviates the formation of insoluble magnesium oxychloride, which is apt to be formed when magnesium is used for the reduction, and which has to be removed by addition of sulphuric acid and the excess of acid subsequently neutralised by calcium carbonate.

Lindo-Gladding's method for the determination of potassium in potassium salts, which is much used in the United States, has not given very satisfactory results in the hands of most chemists.<sup>4</sup> In this method the initial conversion of the sulphates in kainite or in other potassium salts containing sulphate, into the corresponding chlorides, is avoided by taking a measured portion (0.5 g. in solution) and treating it with 0.25 g. of sodium chloride and a few drops of hydrochloric acid, evaporating with 15 c.c. of platinic chloride solution (1 : 10), washing the residue with alcohol (80 per cent.) till free from sodium

<sup>1</sup> *Z. anal. Chem.*, 1893, 32, 184.

<sup>2</sup> *Chem. Zeit.*, 1896, 20, 502.

<sup>3</sup> *Ibid.*, 1898, 22, 99.

<sup>4</sup> Cf. Breyer and Schweitzer, *Z. anal. Chem.*, 1896, 35, 687; and, Robinson, *J. Amer. Chem. Soc.*, 1894, 16, 364.

platinichloride, and finally with an ammonium chloride solution prepared as follows:—"To a solution of 100 g. of ammonium chloride in 500 c.c. of water 10 g. of potassium platinichloride are added, and after frequent vigorous shaking at intervals during six to eight hours, allowed to stand over night, and filtered." The potassium platinichloride is washed quite free from sulphates with this solution, then again with 80 per cent. alcohol, and finally dried and weighed.

For manures of complicated composition containing potassium, Schweitzer and Lungwitz<sup>1</sup> use a solution of barium oxalate in hydrochloric acid for the precipitation of the sulphuric and phosphoric acids, and remove the alkaline earths as oxalates and the iron and aluminium as hydroxides by the addition of hydrogen peroxide and ammonia. In place of barium oxalate, A. Mayer<sup>2</sup> proposes the use of equivalent solutions of barium chloride and oxalic acid; he adds barium chloride from a measuring cylinder till no further precipitate is produced, and then an amount of oxalic acid corresponding to the barium chloride used.

Gilbert<sup>3</sup> precipitates the potassium with excess of cobaltous acetate and sodium nitrite as potassium sodium cobalt nitrite, washes the precipitate first with a cobalt solution (10 g. crystallised cobaltous acetate and 90 g. pure potassium-free sodium nitrite dissolved in water, 25 c.c. acetic acid (sp. gr. 1.04) added, and the solution made up to 1 litre), and finally with 80 per cent. alcohol. The washed precipitate is then either dissolved by warming with hydrochloric acid, or decomposed at 300° and the residue taken up with water. The solution thus obtained is then further treated, as usual, with platinic chloride or with perchloric acid. However accurate this method may be, the lengthy manipulation involved renders it unsuited to technical purposes.

The following method is recommended by Neubauer<sup>4</sup>:—Twenty-five c.c. (=0.5 g.) of an aqueous solution of the potassium salt prepared in the usual way, are evaporated nearly to dryness on the water-bath in a large porcelain dish with a slight excess of platinic chloride and a few drops of hydrochloric acid. On cooling, the mass is moistened with about 1 c.c. of water, vigorously rubbed with a thick glass rod, and the titration repeated after each of three separate additions of 10 c.c. of alcohol (93 to 96 per cent. by vol.). After standing covered for half an hour, during which time the precipitate is rubbed up again several times, the contents of the dish are filtered through a Gooch crucible lined with asbestos. The whole of the precipitate is washed on to the crucible with alcohol, the alcohol washed out with ether, and the ether finally

<sup>1</sup> *Chem. Zeit.*, 1894, 18, 1320.

<sup>2</sup> *Z. anal. Chem.*, 1897, 36, 159.

<sup>3</sup> Inaugural dissertation, Tübingen, 1898: *Die Bestimmung des Kaliums nach quantitativer Abscheidung desselben als Kaliumnatriumkobaltnitrit.*

<sup>4</sup> *Chem. Zeit.*, 1894, 18, 1320.



removed by drawing through air. The potassium platinichloride is then reduced by heating the crucible (fitted up as a Rose's crucible with lid, etc.) in a current of coal gas; the reduction is complete in about half an hour. When cold, the contents of the crucible are moistened with cold water, and then washed about fifteen times with successive portions of hot water. Suction is then stopped and the crucible filled with 5 per cent. nitric acid, and kept full of acid by repeated additions during half an hour. The acid is then pumped off and the platinum washed with hot water, dried, ignited, and weighed. The weight of platinum found multiplied by 0.48409 gives the corresponding weight of potassium as  $\text{K}_2\text{O}$ . Although this method possesses points of considerable merit, it cannot, on account of its complexity, hope to replace the ordinary methods used in the potash industry.

## SPECIAL METHODS OF ANALYSIS

### I.—STASSFURT SALTS

#### A. CRUDE SALTS

*Carnallite* (mixture of carnallite, rock salt, and kieserite), *Rock kieserite* (mixture of carnallite and kieserite), *Kainite* (mixture of kainite and rock salt), *Sylvinite* (mixture of sylvite and rock salt), "*Hartsalz*" (mixture of sylvite, rock salt, and kieserite).

For the examination of the crude salts it is well to take as large a sample as possible.

*Determination of Potassium by the Platinum method.* In the Stassfurt laboratories, such quantities of the salts to be examined are weighed out, according to Precht's proposal, that the calculation of the content of potassium chloride or sulphate from the weight of potassium platinichloride precipitate is avoided. One mg. of potassium platinichloride is made to correspond to 0.1 per cent. of potassium chloride or sulphate. Taking the factors<sup>1</sup> for the calculation of the content of potassium chloride, potassium sulphate, or potassium oxide from the potassium platinichloride found as 0.3056, 0.3571, and 0.1931 respectively, suitable multiples of these figures are taken in the original weighings according to whether the percentage of potassium chloride or sulphate is required. This plan has the further advantage that the quantity of platinic chloride to be added is independent of whether the content is calculated to potassium chloride or to potassium sulphate.

<sup>1</sup> These factors are based on the results of prolonged experience at Stassfurt, and are in accord with the most accurate data obtained independently by other investigators. The precipitate obtained is not pure  $\text{K}_2\text{PtCl}_6$ , as it retains some combined water, which is not given up, even on prolonged heating; on this account the factors are somewhat lower than would correspond to the actual atomic weight, 194.80 for platinum.

The method of procedure for the determination of potassium in crude potassium salts is as follows:—30.56 g. of carnallite or of rock kieserite, or 35.71 g. of kainite, sylvite, or hartsalz, are dissolved in a 500 c.c. flask by boiling with 300 c.c. of water with addition of 15 c.c. of concentrated hydrochloric acid, and after cooling diluted up to the mark. Generally, and if the sample is finely ground, 7.640 g. and 8.9275 g. respectively suffice for the analysis. It makes no difference whether the crude salts are dissolved in pure water or in water containing hydrochloric acid, but as hydrochloric acid must be added before precipitating the sulphuric acid, there is no reason why the addition should be deferred until after dissolving. Fifty c.c. of the solution previously filtered, if necessary, are treated in a 200 c.c. flask with barium chloride, as described on p. 536, filled up to the mark after cooling, and 20 c.c. of the filtrate (=0.3056 or 0.3571 g. of substance) evaporated on the water-bath in a flat porcelain dish about 10 cm. in diameter, after addition of a sufficient quantity of platinic chloride. A solution is usually used containing 1 g. of platinum in 10 c.c. For the above quantities 6 c.c. is more than sufficient; this excess is to be recommended, as it facilitates the washing. During evaporation the contents of the dish are frequently agitated and the evaporation continued until the residue is of a syrupy consistency, and hydrochloric acid fumes cease to be evolved. On cooling, the contents solidify to a crystalline mass. The formation of large crystals of sodium platinichloride should be prevented if possible, since they render thorough washing more difficult. The residue is first broken down with a flat-headed glass rod without addition of alcohol, then thoroughly ground up with about 20 c.c. of alcohol, and the washings filtered through a tared filter paper previously dried for about one hour, till constant, at 120° to 130°, weighed warm, and moistened with alcohol before filtering. Since some kinds of filter paper gain weight (2 to 5 mg.) on moistening with alcohol and subsequent drying, it is advisable to moisten the filter with alcohol, and then dry and weigh it before use. Care must be taken in filtering to prevent the liquid from coming in contact with the edge of the filter paper. Two or three similarly conducted washings with alcohol suffice for the complete removal of the soluble platinum double salts. This end is more quickly attained if, after the second addition of alcohol, the dish with its contents are warmed on the water-bath till the alcohol nearly boils. A low result need not be feared from this treatment, since by far the greatest part of the substances which could induce a solvent action of the hot alcohol on the potassium platinichloride is removed by the first cold decantation. The washed precipitate is then brought on to the filter paper, and after as much alcohol has been pumped off as possible, is pressed between filter paper, dried till constant at 120° to 130°, and weighed warm. Twenty minutes generally suffices for the drying.

Before drying, the filter paper is conveniently folded, as shown in Figs. 147 (front view) and 148 (back view); the possibility of any precipitate falling out is thus prevented. One mg. of potassium platinichloride corresponds to 0.1 per cent. of potassium chloride or sulphate.

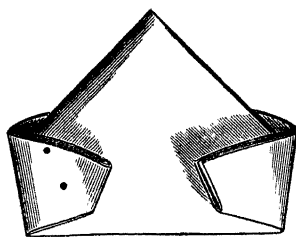


FIG. 147.

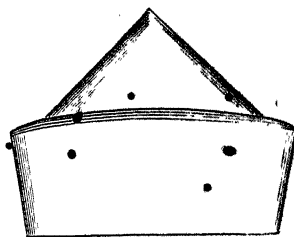


FIG. 148.

*Determination of Potassium by the Perchloric acid method.* 13.455 g. of carnallite or rock kieserite, or 15.7225 g. of kainite, sylvite, or hartsalz, are dissolved by heating to boiling with 300 c.c. of water and 15 c.c. of concentrated hydrochloric acid in a 500 c.c. flask, and barium chloride added as before. In this method a slight excess of barium chloride does not influence the accuracy of the result, since barium chloride is converted by perchloric acid into barium perchlorate, which is readily soluble in alcohol. For the precipitation of the sulphuric acid the quantities of normal barium chloride solution (122 g. of  $\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$ , and 50 c.c. of concentrated hydrochloric acid in 1000 c.c.) required are, for carnallite, about 20 to 40 c.c., and for kainite, 65 to 80 c.c. After cooling, the contents of the flask are made up to the mark and filtered through a double, dry, pleated filter paper about 18 cm. in diameter. Twenty c.c. of the filtrate (0.5382 or 0.6289 g. of substance) are evaporated on the water-bath in a flat, dark-blue glazed porcelain dish 10 cm. in diameter, with 5 c.c. of perchloric acid of 1.125 sp. gr., till the smell of hydrochloric acid ceases and white fumes of perchloric acid are evolved. The residue when cold is carefully triturated with 20 c.c. of 96 per cent. alcohol. After allowing to settle for a short time, the supernatant liquid is filtered through a paper prepared as in the case of the platinum method, or through a Gooch crucible. The trituration is repeated twice, using 96 per cent. alcohol to which 2 per cent. of perchloric acid has been added, in place of pure alcohol. The residue is then removed on to the paper or crucible, and subsequently washed with the mixture of perchloric acid and alcohol. The perchloric acid is finally removed from the filter and precipitate by washing with the smallest possible quantity of pure 96 per cent. alcohol. The precipitate is then dried and weighed as in the platinum method.

One mg. of potassium perchlorate corresponds in this case also to 0.1 per cent. of potassium chloride or sulphate.

*Determination of Magnesium chloride.*<sup>1</sup> The magnesium chloride of carnallite is easily extracted by alcohol, whilst that of kainite is not dissolved. A simple method for distinguishing between "non-carnallitic" crude salts and "carnallitic" salts is based on this difference.

Ten g. of the finely ground crude salt are vigorously shaken for ten minutes in a 250 c.c. flask with 100 c.c. of 96 per cent. alcohol, and 10 or 20 c.c. of the alcoholic filtrate titrated with  $N/10$  silver nitrate solution. Those salts which contain more than 6 per cent. of chlorine soluble in alcohol are classed in as "carnallitic," and those containing 6 and less per cent. as "non-carnallitic."

*Determination of the Total Magnesium.* The following is a very accurate method, introduced by Precht,<sup>2</sup> for the determination of magnesium salts, and is applicable to kieserite: 10 g. of the finely ground crude salt are boiled for not less than one hour in a 500 c.c. flask filled to about two-thirds with water; after cooling, from 50 to 60 c.c. of  $2N$  potassium hydroxide are added, and, in case of a high content of calcium, an additional 20 c.c. of a neutral solution of potassium oxalate (1:10). The flask is then filled up to the mark, and the solution filtered after standing a quarter of an hour. Fifty c.c. of the filtrate are then titrated back with  $N/10$  sulphuric acid. An empirical correction of 1.2 per cent must be added to the content of magnesium sulphate found.

*Volumetric determination of the Sulphuric acid.* The method first worked out by Wolf Mülle,<sup>3</sup> and later in collaboration with K. Dürkes,<sup>4</sup> for the titration of sulphuric acid by means of benzdine hydrochloride, may be used with advantage in the examination of potassium salts. The determinations are reliable, and are quickly and easily carried out (cf. p. 280).

#### COMPLETE ANALYSIS OF THE CRUDE SALTS

One hundred g. of the sample are dissolved in about 500 c.c. of water, the solution filtered, and the filtrate and washings diluted to litre. One portion of the solution is set aside for the determination of the sulphuric acid, and another portion for the estimation of the calcium and magnesium. For the determination of the chlorides of the alkalis, 100 c.c. of the solution (= 10 g. of substance) are acidified with hydrochloric acid, heated to boiling, and the sulphates completely precipitated in a 500 c.c. flask with barium chloride, avoiding an excess of the precipitant. The solution is diluted up to the mark and 50 c.c.

<sup>1</sup> *Z. anal. Chem.*, 1879, 18, 438.

<sup>2</sup> *Ibid.*

<sup>3</sup> *Ber.*, 1902, 35, 1587.

(= 1 g. of substance) evaporated to dryness to drive off the hydrochloric acid, and then the magnesium chloride decomposed by igniting with oxalic acid. After ignition, the residue is moistened with a small quantity of ammonium carbonate, so as to convert the calcium oxide formed into carbonate. The chlorides of the alkalis thus completely freed from calcium and magnesium salts, are dissolved, filtered, and the filtrate evaporated and weighed. The potassium chloride contained in the mixed chlorides is then estimated either by platinic chloride or by perchloric acid in the usual way. The weight of mixed chlorides, less the amount of potassium chloride, gives the content of sodium chloride. The constituents of the crude salts insoluble in water are determined by treating 10 g. of the salt with hot water, filtering off the insoluble matter on to a tared filter paper, which is then dried at  $100^{\circ}$  and weighed. For the determination of water, 10 g. are weighed into a platinum crucible, covered with a weighed quantity of ignited lead oxide, and heated with the lid on for ten minutes over a small flame to a dull red heat; the loss after ignition gives the water content. Or 10 g. are ignited, the loss determined, the ignited mass dissolved in water, and the dissolved chlorine determined volumetrically, in order to find how much magnesium chloride was decomposed by the ignition. The difference between the chlorine content before and after ignition, allowing for the gain in oxygen, is deducted from the loss on ignition; the remainder of the loss is water.

In the case of kainite, the calculation of the salts is effected by subtracting from the total quantity of soluble sulphuric acid the amount of sulphuric acid corresponding to the calcium found. The remaining sulphuric acid is divided into two parts, and calculated to potassium sulphate and magnesium sulphate in the molecular proportions in which these salts are present in kainite and in picromerite respectively. The magnesium not combined as sulphate is calculated as chloride, and any remaining potassium is taken as potassium chloride. These calculations indicate on the one hand how much potassium is present as kainite ( $K_2SO_4 \cdot MgSO_4 \cdot MgCl_2 \cdot 6H_2O$ ), and as picromerite ( $K_2SO_4 \cdot MgSO_4 \cdot 6H_2O$ ), and on the other hand how much is present as potassium chloride. Any sodium present is reckoned as sodium chloride. In hartsalz, in which the water content (up to 5 per cent.) amounts to only about one-third of that in kainite, the potassium is reckoned as chloride. If langbeinite ( $K_2SO_4 \cdot 2MgSO_4$ ) is present as an impurity, the magnesium and any calcium are calculated as sulphates, and any excess of sulphuric acid as potassium sulphate. In dealing with the examination and recognition of complicated mixtures of salts, the determination of the individual constituents does not suffice. In such cases, the amount of magnesium chloride soluble in alcohol must be determined, and the content of carnallite deduced therefrom, and a separation of the con-

stituents by means of specific gravity must also be made. If the individual constituents in the salts of different specific gravity are then determined, the composition of the original mixture can be calculated from that of the different salts. The separation by means of specific gravity is carried out by mixing the fairly finely ground mixture of salts with a solution of benzene and bromoform, so proportioned that the whole of the salts sink to the bottom of the vessel; by gradually increasing the specific gravity of the liquid by the addition of bromoform, the lighter particles rise successively to the top and can be collected.

#### B. INTERMEDIATE PRODUCTS OF MANUFACTURE

The examination of the intermediate products, liquors, residues, etc., arising in the working up of the crude salts into concentrated potassium salts, is carried out by the methods described above for the crude salts. Should these products contain but little potassium and much sodium chloride, Finkener's method of separation may be used with advantage. The solution containing the potassium salts is treated, without previous separation of sulphates, with only just sufficient platinic chloride to precipitate the potassium; after washing the evaporated residue, the potassium platinichloride is reduced and weighed as platinum.

#### C. MANUFACTURED PRODUCTS

##### 1. Potassium Chloride.

*Determination of Potassium by the Platinum method.* 7.640 g. of the finely ground sample are dissolved and made up to 500 c.c. In the case of salts containing more than 0.5 per cent. of sulphuric acid ( $\text{SO}_3$ ), the previous conversion of the sulphates into the corresponding chlorides by means of barium chloride containing hydrochloric acid is necessary. Twenty c.c. ( $=0.3056$  g. of the salt) of the solution or filtrate are then evaporated with 5 c.c. of platinic chloride solution. The evaporation may be continued to dryness without risk; this treatment differs from that of the crude salts, since, together with the potassium platinichloride, which constitutes the bulk of the residue, only sodium platinichloride is present, which is more readily dissolved by alcohol when dehydrated than when hydrated.

The further treatment of the residue is carried out as described for the crude salts. The use of hot alcohol for washing is in this instance also to be strongly advocated. One mg. of potassium platinichloride corresponds to 0.1 per cent of potassium chloride.

*Determination of Potassium by the Perchloric acid method.* 13.455 g. of the finely ground sample are dissolved in water; 3 to 4 c.c. of barium

chloride solution containing hydrochloric acid (122 g.  $\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$  dissolved in water, and after addition of 50 c.c. concentrated hydrochloric acid diluted to 1000 c.c.) added, and the whole then made up to 500 c.c. To 20 c.c. (= 0.5382 g. of the salt) of the filtrate are added one and a half times the quantity of perchloric acid necessary for the decomposition of all the salts, the solution evaporated on the water-bath, and the residues treated as described under "Crude Salts." One mg. of potassium perchlorate corresponds to 0.1 per cent. of potassium chloride.

*Determination of the Sodium chloride in high percentage Potassium chloride.* The following method for the determination of the sodium chloride should only be used in dealing with 95 to 99 per cent. potassium chloride. It is a modification of the method recommended by Röttger and Precht,<sup>1</sup> and depends on the greater solubility of sodium chloride in alcohol as compared with that of potassium chloride. The solubilities are as follows:—

At 15°, 100 parts of alcohol of:—

	90 per cent.	92.5 per cent.	95 per cent. by weight
dissolve	0.345	0.223	0.146 parts of sodium chloride
and	0.073	0.043	0.028 parts of potassium chloride.

According to the Röttger-Precht method, 20 g. of the finely ground potassium chloride are vigorously shaken for half an hour in a 100 c.c. flask with about 80 c.c. of 90 per cent. alcohol. Any magnesium salts present are precipitated by the addition of 0.5 c.c. of a 10 per cent. potassium carbonate solution, the whole again vigorously shaken and made up to the mark with 90 per cent. alcohol. Fifty c.c. (= 10 g. of the salt) are evaporated to dryness in a platinum dish, gently ignited, and weighed; the potassium chloride is determined in the residues, and the sodium chloride present in the original salt estimated by difference.

In order to obviate the prolonged shaking of the salt with 90 per cent. alcohol and at the same time to bring about rapid solution of the sodium chloride, the following procedure is adopted in the laboratories of the German Potash Syndicate:—

12.5 g. of potassium chloride are dissolved in a 255 c.c. flask by boiling with 25 c.c. of water in which about 90 mg. of potassium carbonate are dissolved. A larger excess of potassium carbonate may bring about a partial re-separation of the dissolved sodium chloride. Absolute alcohol is added to the hot solution, the whole well mixed, made up to the mark, and shaken vigorously for about one minute. One hundred c.c. (= 5 g. of salt) of the filtered solution are evaporated to dryness in a platinum or porcelain dish, after addition of a few drops of concentrated hydrochloric acid to neutralise the dissolved potassium carbonate. The

<sup>1</sup> Ber., 1885, 18, 2076.

residue is then gently ignited and weighed. In the mixture of potassium and sodium chlorides thus obtained, the potassium chloride is either determined by means of platinic chloride or perchloric acid and the sodium chloride taken by difference, or the total chlorine content is estimated volumetrically by titration with  $N/10$  silver nitrate solution, and the amount of potassium chloride and sodium chloride calculated indirectly.

*Determination of Magnesium chloride or of Magnesium salts in Potassium chloride.* To arrive at the content of magnesium salts or of magnesium chloride in potassium chloride, 25 g. of the salt are dissolved in a 500 c.c. flask and 10 c.c. of  $2N$  potassium hydroxide added. After filling up to the mark, shaking and filtering, 50 c.c. of the filtrate are titrated with  $N/10$  sulphuric acid. Any calcium compounds remaining in solution do not influence the result.

The precipitation of the magnesium salts by means of calcium saccharate, whereby magnesium oxide and not magnesium saccharate is formed, may also be used for the determination. This method is adopted at the Salzbergwerk Neustassfurt. The procedure is as follows:—

Twenty-five g. of the salt are treated with 150 to 200 c.c. of water in a 250 c.c. flask, 25 c.c. of a calcium saccharate solution of known strength added, the whole well shaken and diluted to 250 c.c. The bulky precipitate of magnesia is filtered off after a short time through a pleated filter paper, and 50 c.c. of the filtrate titrated with  $N/10$  sulphuric acid, using phenolphthalein as indicator.

The calcium saccharate solution is best prepared by adding 450 g. of calcium oxide and 450 g. of sugar to 7 litres of water; after shaking vigorously for half an hour the precipitate formed is allowed to settle for from two to three weeks, then filtered, and a further 450 g. of sugar added. Access of air should be avoided both in the use and in the storage of the solution.

*Determination of Water.* This determination is carried out in the same manner as that described for the crude salts, except that the covering layer of lead oxide is only employed in the case of salts rich in magnesium chloride.

*Determination of Insoluble Matter.* To estimate the ingredients insoluble in water, 10 g. of potassium chloride are dissolved in hot water, and the residue collected on a tared filter paper.

The determinations of *Calcium* and of *Sulphuric acid* are carried out by the ordinary methods.

## 2. Potassium Sulphate.

*General considerations on the analysis of Potassium salts containing a high percentage of Sulphates.* In the determination of potassium in



compounds containing a high percentage of sulphates, provided the potassium is to be separated as platinichloride or perchlorate, the most difficult part of the analysis lies in the precipitation of the sulphuric acid by means of barium chloride. In the case of the platinum method, a small amount (about 0.5 per cent. of  $\text{SO}_3$ ) of unprecipitated sulphate does not matter, since, as stated above, an excess of barium chloride is to be avoided at all costs on account of the decomposition of barium platinichloride by alcohol. On the other hand, a small excess of barium chloride does not influence the result when the perchloric acid method is employed. The considerations which have been urged against the method used at Stassfurt for the precipitation of the sulphuric acid are not warranted. If the instructions given below are carefully carried out, an easy and complete separation of the sulphuric acid is effected and accurate results are obtained. In order to prevent the possibility of the barium sulphate carrying down any potassium, the precipitation is effected in a strong hydrochloric acid solution (122 g.  $\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$ , with 50 c.c. concentrated hydrochloric acid, diluted to 1000 c.c.); the barium chloride must be free from potassium salts as impurities. In the laboratory of the "Konsolidierte Alkaliwerke zu Westeregeln," the conversion of the sulphates in the crude salts into the corresponding chlorides is carried out in neutral solution as follows: 10 g. of carnallite with about 150 c.c. of water are brought to the boil in a 250 c.c. flask and precipitated with a neutral solution of 127 g.  $\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$  in 1 litre (1 c.c. = 50 mg.  $\text{SO}_4$ ), which is run in from a burette. The advantage of using this neutral solution is, that a direct indication is given of the point at which complete precipitation of the sulphuric acid has taken place. This is shown by the appearance of the steam bubbles, which remain transparent until the precipitation is complete and then suddenly become opaque. As a precaution, a few more drops of barium chloride solution are then added. After cooling, the flask is filled up to the mark. The errors arising from ignoring the volume of the barium sulphate and from the precipitation being effected in neutral solution compensate one another.

*Determination of Potassium by the Platinum method.* 8.9275 g. of the finely ground sample are dissolved by boiling in 350 c.c. of water and 20 c.c. of concentrated hydrochloric acid, in a 500 c.c. flask. To the boiling solution barium chloride is then run in, drop by drop, from a stoppered burette. From the composition of the potassium salt under analysis the amount of barium chloride required for the precipitation of the sulphuric acid is approximately calculated beforehand, so that the greater part of the barium chloride can be added without testing. The final additions are made carefully, and the solution tested from time to time to see how far the precipitation has proceeded. The complete precipitation of the sulphuric acid is most sharply recognised by adding a crystal of barium

chloride to the clear, settled solution and noting whether any milkiness is produced. Should a trace of sulphuric acid still be present, the crystal produces a distinct cloudiness which spreads gradually throughout the solution from top to bottom. Any slight excess of barium chloride is removed by the addition of a few drops of sulphuric acid. When the precipitation is complete and the solution cold, the flask is filled up to the mark and 20 c.c. ( $=0.3571$  g. of the salt) of the filtered solution treated as usual with 5 c.c. of platinic chloride solution (1 : 10). One mg. of potassium platinic chloride corresponds to 0.1 per cent. of potassium sulphate. To the amount of potassium sulphate found, 0.3 per cent. must be added in the case of potassium sulphate (90 to 97 per cent.); no correction is necessary with potassium magnesium sulphate.

*Determination of Potassium by the Perchloric acid method.* 15.7225 g. of the salt are dissolved by boiling in 700 c.c. of water and 30 c.c. of concentrated hydrochloric acid in a litre flask; a 500 c.c. flask is not sufficiently large, on account of the considerable bulk of the barium sulphate precipitate. The further manipulation is the same as given above, with the exception that a smaller excess of barium chloride may be employed, and instead of 20 c.c., 40 c.c. of the filtrate ( $=0.6289$  g. of the salt) are evaporated with the necessary quantity of perchloric acid. One mg. of potassium perchlorate corresponds to 0.1 per cent. of potassium sulphate. To the content of potassium sulphate found, 0.3 per cent. must be added, as above.

The less important constituents of the potassium sulphate or potassium magnesium sulphate (magnesium, calcium, sodium, sulphuric acid, chlorine, water, and insoluble matter) are determined by the usual methods.

### 3. Potassium Salt Manures.

The analysis of potassium salt manures does not differ essentially from that of potassium sulphate. According as to whether the potassium content is to be expressed as potassium chloride or as sulphate, either 15.280 g. (if as chloride) or 17.855 g. (if as sulphate) of the salt are taken if the potassium is estimated as platinichloride. Should the perchloric acid method be preferred, the quantities taken are correspondingly altered. The potassium salt manures frequently contain a large amount of matter insoluble in hydrochloric acid, which renders the end-point in the precipitation of the sulphuric acid difficult to recognise, in which cases it is advisable to filter the hydrochloric acid solution before precipitating. The procedure, using the platinum method, is then as follows:—

15.280 g. or 17.855 g. of the sample are dissolved in water with addition of 10 c.c. of concentrated hydrochloric acid in a 500 c.c. flask, diluted to the 500 c.c. mark, shaken, filtered, and 250 c.c. ( $=7.640$  g. or

8.9275 g. of the salt) of the filtrate precipitated with barium chloride, as usual, in a 500 c.c. flask, made up to 500 c.c., shaken, filtered, and 20 c.c. of the filtrate evaporated with 6 c.c. of platinic chloride solution (1 : 10). No addition to the content of potassium chloride or sulphate found is necessary.

The estimation of the remaining constituents is carried out by any of the above methods. In the determination of moisture a possible high content of magnesium chloride must be borne in mind.

## II.—NITRE

### A. RAW MATERIALS

#### 1. Chili Saltpetre.

The methods of analysis are given on p. 306 *et seq.*

#### 2. Potassium Chloride.

The potassium chloride used for the preparation of nitre contains at least 80 per cent. of potassium chloride and not more magnesium salts than correspond to 0.5 per cent. of magnesium chloride. For the methods of analysis, see p. 533 *et seq.*

### B. INTERMEDIATE PRODUCTS

The analytical methods of examination for the solid, intermediate products of the semi-refined nitre are the same as those applied to Chili saltpetre. The foreign materials, water, insoluble matter, sodium chloride, and sulphates (seldom present, or only in traces) are estimated, and the difference taken as potassium nitrate.

The analysis of the saltpetre liquors is somewhat more detailed, and primarily demands a determination of the neutrality of the liquors, *i.e.* whether they contain an excess of sodium nitrate or of potassium chloride. This necessitates an estimation of the potassium and of the nitric acid. The potassium is determined by accurately precipitating the sulphuric acid in 20 c.c. of the liquor in a 250 c.c. flask by means of barium chloride, filling to the mark, and evaporating 10 c.c. of the filtrate with the requisite quantity of platinic chloride. The potassium found is calculated to potassium nitrate.

The nitric acid is estimated by any of the usual methods (*cf.* p. 309 *et seq.*), and is calculated to potassium nitrate. From the amounts of potassium and nitric acid found it is easy to determine whether the liquors contain an excess of sodium nitrate or of potassium chloride.

The determination of iodine in the liquors is carried out by first add-

ing 20 c.c. of carbon bisulphide to 20 c.c. of the liquor, in a separating funnel of about 200 to 250 c.c. capacity, and then a small quantity of fuming nitric acid or of sulphuric acid to set free the iodine, which is extracted by shaking up with the carbon bisulphide. The latter is separated, washed with water in a second separating funnel, and then titrated with  $N/10$  sodium thiosulphate. Or the iodine in 20 c.c. of the liquor is precipitated by copper sulphate as cuprous iodide, the precipitate washed with hot water, and the iodine determined by ferric ammonium alum and sulphuric acid.

The waste salt (sodium chloride) arising from the decomposition of Chili saltpetre by means of potassium chloride retains some 1 to 3 per cent. of undecomposed potassium chloride and small quantities of potassium nitrate (0.25 to 0.75 per cent.), which are not removed by further washing. The contained potassium is determined in the usual manner by means of platinic chloride. For the determination of the nitric acid, 50 g. of the waste salt are dissolved and made up to 500 c.c., and 50 c.c. of the solution (= 5 g. of the salt) used for the estimation.

### C. FINAL PRODUCT (NITRE)

The refined nitre should be free from all impurities except a small proportion of chloride. The content of sodium chloride is generally guaranteed less than 0.003 per cent. The moisture should not be above 0.25 per cent.

The nitre is tested as follows:—

*Moisture.* Ten g. of nitre are dried at  $120^{\circ}$  to  $130^{\circ}$  for two hours.

*Chlorine.* One hundred g. of nitre are dissolved in water, silver nitrate added, and the precipitate either weighed or the cloudiness compared with that produced on titrating a standard sodium chloride solution with silver nitrate.

*Insoluble impurities.* Sulphates, calcium, and magnesium are determined by the usual methods; sodium with potassium metantimonate. Not less than 100 g. of nitre are taken for each determination.

Any small content of *Perchlorate* (guaranteed as from 0.1 to 0.5 per cent. at the maximum) is determined according to one of the methods given under Chili saltpetre (p. 319).

*Potassium chlorate.* Ten g. of the finely ground nitre are stirred with 20 to 25 c.c. of pure concentrated sulphuric acid in a porcelain dish cooled with water. The acid should remain absolutely colourless and show no yellow coloration.

*Iodine.* Small quantities of iodine compounds which may sometimes be present, are recognised by the so-called vapour test. Three g. of the substance to be tested are placed in a dry, perfectly clean test tube, 14 to 15 mm. in diameter and 135 to 140 mm. long. Any substance

sticking to the walls of the tube must be removed as completely as possible by means of filter paper. The test tube is closed by a rubber stopper with one hole, through which a glass rod is inserted, fitted at the end with a hook of platinum wire. A strip of filter paper 2 cm. long by 1 cm. broad, the upper half of which is moistened with a solution of one part of chemically pure glycerine in one part of water, is attached to the hook, and suspended so that the bottom edge is 40 mm. above the substance. The test tube is then placed in a water-bath at  $71^{\circ}$  to  $72^{\circ}$ ; the temperature must be kept constant during the whole of the experiment. The test is finished after the recognised time of heating is completed, or after the characteristic coloration of the test paper has appeared, a faint yellow mark at the junction of the dry and moistened portions of the paper. On allowing the test tube to remain longer in the water-bath, the faint yellow colour passes gradually through brown to a deep brown. Care must be taken to keep the water-bath filled to just within the edge.

### III.—POTASSIUM CARBONATE

#### A. RAW MATERIALS

##### 1. Potassium Chloride.<sup>1</sup>

Potassium chloride from beet ashes contains fairly large quantities of sulphate and some carbonate. The potassium, chlorine, sulphuric acid, and alkalinity are determined and the contents of the several constituents calculated from these estimations.

In the case of sulphate recovered from beet ashes, which contains potassium chloride, and potassium and sodium carbonates, the several constituents are estimated in a similar manner by determining the total alkali, sulphuric acid, chlorine, and potassium. The chlorine and sulphuric acid are calculated to potassium chloride and sulphate, the potassium contained in these salts deducted from the total potassium, and the remaining potassium taken as potassium carbonate; the difference between the alkali corresponding to the potassium carbonate and the total alkali is calculated as sodium carbonate.

##### 2. Beet Ashes.

On account of the very deliquescent nature of beet ashes, the sample ground in a warm mortar.

*Moisture.* Six to 10 g. of the powdered sample are placed between previously weighed pair of ground watch-glasses, the glasses with sample accurately weighed, and dried at  $140^{\circ}$  till constant.

<sup>1</sup> *G. I., C.*, p. 533.

*Insoluble matter.* For the determination of the matter insoluble in water and the inorganic residue left after lixiviation, 20 g. of the powdered substance are weighed quickly but accurately on a clock-glass transferred carefully into a large beaker or deep porcelain dish containing 150 c.c. of hot water, boiled up, and heated for fifteen minutes with continual agitation. The solution is filtered hot into a 500 c.c. flask through a previously weighed filter paper, and dried at 130°. A further 120 c.c. of boiling water are added to the residue, the whole again boiled up, and the solution decanted through the filter paper. The residue is then brought on to the paper, washed with boiling water till the total filtrate and washings are nearly up to the 500 c.c. mark of the flask, or till the filtrate commences to run through milky; the residue and paper are dried at 120°, placed between the ground clock-glasses whilst hot allowed to cool in a desiccator, and weighed. The gain in weight gives the total matter insoluble in water. After weighing, the residue is detached from the paper and gently ignited in a large platinum dish till all the carbonaceous matter is completely ashed; the filter paper is ignited apart in the same dish. The residue remaining in the dish is the inorganic lixiviation residue, and the loss on ignition the organic matter.

The cooled filtrate (the beet ash solution) is made up to exactly 500 c.c. with distilled water, and serves for the subsequent determinations.

*Alkali salts.* Twenty-five c.c. of the solution (corresponding to 1 g. of beet ashes) are pipetted off into each of four small porcelain dishes and each weighed, together with a small glass rod. The solutions are evaporated to dryness on the water-bath, being stirred continually with the glass rods, the dishes covered with previously warmed watch-glasses, ignited over a free flame, allowed to cool in a desiccator, and weighed. The increase in weight gives the total alkali, the mean of the four determinations being taken as the result. The residues so obtained are used for determining the alkalinity, the potassium chloride, and the total potassium.

*Alkalinity and Potassium chloride.* The contents of one of the dishes (= 1 g. of beet ashes) is dissolved in cold water, washed into a beaker, and titrated with normal nitric acid, using methyl orange as indicator. The number of c.c. used multiplied by 6.915 gives the percentage of alkalinity, expressed as  $K_2CO_3$ .

The neutralised solution is heated to boiling to drive off any hydrocyanic acid, and after cooling titrated with  $N/10$  silver nitrate, a few drops of potassium chromate being added as indicator. The number of c.c. of silver nitrate used multiplied by 0.7460 gives the percentage of  $KCl$ , and multiplied by 0.6915 the corresponding percentage of  $K_2CO_3$ .

*Potassium sulphate and Potassium sulphide.* (a). *Total Potassium sulphate* (from the total sulphur content). Twenty-five c.c. of the

filtrate from the "insoluble matter" (1 g. beet ashes) are diluted in a beaker with about 75 c.c. of water, excess of bromine water added, and the solution heated and kept boiling for about a quarter of an hour. The solution should contain excess of bromine after boiling. After saturating with hydrochloric acid and heating till the smell of bromine has completely disappeared, barium chloride solution, previously brought to boiling in a test tube, is added. The number of mg. of  $\text{BaSO}_4 \times 0.7468$  gives the percentage of  $\text{K}_2\text{SO}_4$  (the total sulphur compounds calculated as  $\text{K}_2\text{SO}_4$ ), and the mg.  $\text{BaSO}_4 \times 0.5924$  the corresponding percentage of  $\text{K}_2\text{CO}_3$ .

(b). *Potassium sulphate.* The sulphuric acid in 25 c.c. of the solution from the "insoluble matter" (corresponding to 1 g. of beet ashes) is precipitated in the usual way (without previous addition of bromine), after addition of hydrochloric acid. The mg.  $\text{BaSO}_4 \times 0.7468$  gives the percentage of  $\text{K}_2\text{SO}_4$  as such in the beet ashes, and the mg.  $\text{BaSO}_4 \times 0.5924$  the percentage of  $\text{K}_2\text{CO}_3$  corresponding to the  $\text{K}_2\text{SO}_4$ .

(c). *Calculation of the Potassium sulphide.* The mg. of  $\text{BaSO}_4$  found under (b) subtracted from those found under (a) multiplied by 0.4727 gives the percentage of  $\text{K}_2\text{S}$ , and multiplied by 0.5924 the corresponding percentage of  $\text{K}_2\text{CO}_3$ .

*Potassium phosphate.* Two hundred and fifty c.c. of the filtrate from the "insoluble matter" (= 10 g. of beet ashes) are acidified with nitric acid, and after addition of 10 g. of ammonium nitrate the phosphoric acid is precipitated by means of ammonium nitro-molybdate and weighed as magnesium pyrophosphate. The mg. of  $\text{Mg}_2\text{P}_2\text{O}_7 \times 0.1908$  gives the percentage of  $\text{K}_3\text{PO}_4$ , and the percentage of  $\text{K}_3\text{PO}_4 \times 0.9765$  the corresponding quantity of  $\text{K}_2\text{CO}_3$ .

*Potassium carbonate.* The ignited residue in one of the porcelain dishes from the "alkali salts" determination (containing the alkali salts from 1 g. of beet ashes) is washed with hot water into a 100 c.c. flask, acidified with hydrochloric acid, and precipitated with barium chloride so as to leave a small amount of potassium sulphate unprecipitated, thus making sure of the filtrate being free from barium. After the addition of the barium chloride, and boiling for five minutes, the precipitate is allowed to settle for at least three hours. The contents of the flask are then made up to the mark, well mixed by shaking, and filtered through a dry filter paper. Twenty c.c. of the filtrate (= 0.2 g. of beet ashes) are evaporated in a porcelain dish with 10 c.c. of a 10 per cent. platinic chloride solution, and treated as usual. The number of mg. of  $\text{K}_2\text{PtCl}_6$  found  $\times 0.1416$  gives the percentage of total  $\text{K}_2\text{CO}_3$ . From this value the percentages of  $\text{K}_2\text{CO}_3$  corresponding to the  $\text{KCl}$ , total  $\text{K}_2\text{SO}_4$  and  $\text{K}_3\text{PO}_4$  have to be deducted. The difference is the actual percentage of  $\text{K}_2\text{CO}_3$  contained in the beet ashes.

*Calculation of the Sodium carbonate.* The percentage of  $\text{K}_2\text{CO}_3$ ,  $\text{KCl}$ ,

total  $K_2SO_4$  (not  $K_2SO_5 + K_2S$ , since in the weighed calcined alkali salts the  $K_2S$  is already converted into  $K_2SO_4$ ), and  $K_3PO_4$  are added together, and the sum (the percentage of all the potassium salts) so obtained is deducted from the percentage of alkali salts obtained in the determination of the "alkali salts," as above. The difference, alkali salts less potassium salts, gives the percentage of  $Na_2CO_3$ .

## B. INTERMEDIATE PRODUCTS

### Carbonated Liquors.

The methods given under "Sodium carbonate," p. 429, are applicable.

## C. FINAL PRODUCTS AND BY-PRODUCTS

### 1. Potassium Carbonate (96 to 98 per cent.).

The sample to be examined is well mixed, and ground as quickly as possible in a perfectly dry, preferably iron, mortar. It is then filled into dry bottles and immediately corked. The corks are best rendered air-tight by hot paraffin wax, since even sealing-wax does not prevent the sample absorbing a little moisture on long standing.

*Moisture.* Ten g. of the sample are heated in a platinum crucible till the weight is constant.

*Insoluble matter.* Ten g. of the carbonate are dissolved and warmed in a beaker, the insoluble matter filtered off on to a small filter paper, washed with hot water, ignited, and weighed. Or the residue may be collected on a weighed filter paper and dried at  $100^\circ$ .

*Potassium chloride.* Two g., or in the case of a very pure sample 10 g., are carefully neutralised in a beaker with nitric acid, a drop of methyl orange being added to indicate neutrality, and titrated with  $N/10$  silver nitrate, using potassium chromate as indicator. To obtain a sharp end-reaction, the solution to be titrated should be just alkaline rather than acid.

*Potassium sulphate.* Ten g. of the carbonate are dissolved in hydrochloric acid, filtered, heated to boiling, and precipitated with barium chloride.

*Potassium silicate.* Five g. of the sample are dissolved in water, filtered, the filtrate acidified with hydrochloric acid and evaporated to complete dryness, with stirring, in a platinum dish. The residue is taken up with hydrochloric acid and warmed, diluted with water, and the silica filtered off and determined in the usual way.

*Total Alkali.* Five g. of the potassium carbonate are accurately weighed, dissolved in a 500 c.c. flask, and the solution diluted to the mark. Twenty-five c.c. ( $\approx 0.25$  g.) are titrated in the cold with  $N/10$



sulphuric acid, two drops of methyl orange (1 g. of methyl orange in 1000 c.c. of water) being added as indicator. The complete neutralisation is accurately recognised by adding the sulphuric acid drop by drop; the end-reaction is reached when the solution begins to change from yellow to bright rose colour. The sulphuric acid is accurately standardised in a similar manner against chemically pure anhydrous potassium carbonate.

*Sodium carbonate.* The ash is evaporated with hydrochloric acid and treated with barium chloride; this converts the carbonates into the corresponding chlorides. The contained sodium chloride is then determined by the method given on p. 534.

Fresenius has made use of the following methods to determine the sodium carbonate in the potassium carbonates (96 to 98 per cent. with 0.11 per cent.  $\text{Na}_2\text{CO}_3$ ) produced at the Salzbergwerk Neustassfurt:—

(a) Fifty c.c. of the carbonate solution, corresponding to 1 g. of substance, are acidified with hydrochloric acid, and the sulphuric acid present precipitated with a calculated quantity of barium chloride. The barium sulphate is filtered off, washed, and the filtrate evaporated to dryness in a weighed platinum dish. The chlorides of the alkalis are weighed after gentle ignition. The potassium is then separated as usual with platinic chloride, the potassium platinichloride filtered off and washed, the filtrate along with the washings evaporated to dryness, the residue gently ignited in a current of hydrogen and extracted with water. The solution thus obtained is again treated with platinic chloride, and a further small quantity of potassium platinichloride separated. The filtrate and washings are again evaporated, the residue reduced, extracted with water, the solution evaporated in a platinum dish, and the sodium chloride weighed, after gentle ignition. The sodium chloride is quite free from barium salts. The purity of the reagents used should be ascertained by carrying out a blank experiment.

(b) Ten g. of potassium carbonate are dissolved in water, neutralised with the calculated quantity of chemically pure tartaric acid and then an equal quantity of tartaric acid added, with stirring. After standing for some time any separated tartaric acid is filtered off and completely washed with a small quantity of cold water. The filtrate and washings are evaporated to a small bulk, any tartaric acid separating on standing for a short time, filtered off, washed with a little water, and the filtrate and washings evaporated to dryness in a platinum dish. The residue is gently ignited, dissolved in water to which a little hydrochloric acid has been added, the sulphuric acid carefully precipitated with barium chloride, and the excess of barium removed by addition of ammonium carbonate. The filtrate, together with washings, is evaporated in a platinum dish, the residue gently ignited, dissolved in water, the

potassium separated with platinic chloride, and the sodium determined in the filtrate according to the method given under (a).

In calculating the results it is assumed that the sulphuric acid, silica, and the chlorine are combined with potassium, the sodium present being reckoned as sodium carbonate. The amount of potassium carbonate corresponding to the sodium carbonate and potassium silicate found, is deducted from the total alkali, and the remainder calculated as potassium carbonate.

To control the working conditions in the course of manufacture, the alkali in a potassium carbonate is determined directly by titrating 2.5 g. with sulphuric acid. If a quick and accurate determination is desired, it is preferable to weigh out the required amount of substance for each individual determination, rather than to make up one amount to a definite volume and measure off aliquot parts of the solution for the estimation; this method possesses also the advantage that the most suitable conditions of concentration, etc., for rapid working can be chosen.

## 2. Impure Potassium Carbonate, Molasses Carbonate, and Beet Ash Carbonate.

These carbonates contain, as a rule, potassium phosphate in addition to the constituents mentioned above. The latter are determined by the methods described; the phosphate is an important indication of the origin of the carbonate. Other constituents that occur are potassium hydroxide and various sulphur and cyanogen compounds; these are determined by the methods given under beet ashes (p. 540) and soda vat liquors (p. 426).

*Phosphoric acid.* Five g. of the sample are dissolved in nitric acid, the solution filtered, warmed, and precipitated with ammonium molybdate; the precipitate is then dissolved in ammonia, reprecipitated with magnesium mixture, filtered, ignited, and weighed as usual.

## 3. Hydrated Potassium Carbonate.

This is examined similarly to 96 to 98 per cent. potassium carbonate (cf. C. I, p. 543).

## CYANOGEN COMPOUNDS<sup>1</sup>

By Dr H. FREUDENBERG, Chemist to the Deutsche Gold- und Silber-scheideanstalt, Frankfurt a/M. English translation, revised by JAMES T. CONROY, B.Sc., Ph.D.

### I. SIMPLE CYANIDES

Cyanogen present in combination as hydrocyanic acid, or as alkaline or alkaline-earth cyanide, may be estimated either gravimetrically or volumetrically; in commercial work the volumetric method is generally adopted.

#### I. GRAVIMETRIC METHODS OF ANALYSIS

Cyanogen is determined gravimetrically, either directly as silver cyanide, or indirectly by weighing the silver obtained therefrom. In carrying out this estimation, the pure aqueous solution of hydrocyanic acid or of cyanide is rendered slightly acid by addition of nitric acid—the quantity of free nitric acid present in the solution must not exceed 2 per cent.—and the acidified solution added to a solution of silver nitrate. The separated silver cyanide is allowed to settle, without warming, collected on a tared filter paper, washed, dried at 100°, and weighed. The silver cyanide may, according to Rose, be converted into metallic silver by heating it in a porcelain crucible for fifteen minutes at a red heat. Liebig<sup>2</sup> and Gregor<sup>3</sup> state that the results obtained by this method agree very well with those obtained by volumetric analysis.

Should chlorine, bromine, or iodine be present, the silver cyanide must be separated from the simultaneously precipitated silver haloid. This is effected by means of an acetic acid solution of mercuric oxide, prepared by warming precipitated mercuric oxide with dilute acetic acid. On boiling the mixed silver salts with this solution, the silver cyanide is decomposed with the formation of mercuric cyanide and silver acetate, which goes into solution. The solution of silver acetate is then

<sup>1</sup> This section is based on that by the late C. Moldenhauer in the previous German edition. *Annalen*, 1851, 77, 102.

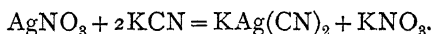
<sup>2</sup> *Z. Anal. Chem.*, 1894, 33, 20.

separated from the residual, undissolved silver salts by filtration, and the contained silver estimated either as silver chloride or as metallic silver. For the latter estimation the chloride is reduced in a current of hydrogen, the usual precautions must be observed for the separation of silver from mercury. The conversion of the chloride into metallic silver is advisable, owing to the tendency of the chloride to carry down some mercury which is not completely volatilised by simple ignition; high results are accordingly likely to be obtained by weighing the chloride.

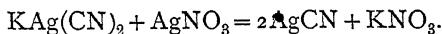
The following example will serve to show the accuracy of this method:—0.1 g. of sodium chloride, 0.1 g. of potassium iodide, and 0.1 g. of potassium cyanide were dissolved in water, the mixture rendered slightly acid by addition of nitric acid, and treated with silver nitrate in slight excess. The resulting precipitate was, after washing, boiled with about 100 c.c. of water and 5 c.c. of acetic acid, in which precipitated mercuric oxide had been dissolved, and the solution separated from the insoluble residue by filtration and washing. The filtrate and washings were treated with nitric and hydrochloric acids, and the precipitated silver chloride ignited in a current of hydrogen. The metallic silver obtained weighed 0.168 g., corresponding to 0.0404 g. cyanogen instead of the 0.0400 g. taken.

## 2. VOLUMETRIC METHODS OF ANALYSIS

1. *Liebig's Method.* This method has been proved by long experience to be thoroughly reliable, and is now generally adopted in technical work. It depends on the fact that when an aqueous solution of potassium cyanide is treated with silver nitrate solution a soluble double salt, potassium silver cyanide, is first produced:—

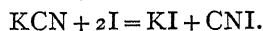


When, however, excess of silver nitrate has been added, this soluble double salt is decomposed with the separation of insoluble silver cyanide, the presence of a very small quantity of which is at once indicated by the solution becoming turbid:—



The manner of carrying out the test is described later (p. 548).

2. *Fordos and Gélis' Method.*<sup>1</sup> This method, which has not as yet found much acceptance in practice, is based on the behaviour of iodine towards potassium cyanide. Serrullas and Wöhler have shown that two equivalents of iodine interact with one equivalent of cyanogen, hydrocyanic acid, or potassium cyanide according to the equation:—



<sup>1</sup> *J. prakt. Chem.*, 1899, 59, 255.

The iodine may be employed in the form of an  $N/10$  solution.

The method gives fairly accurate results if carried out in the manner described below.

### Hydrocyanic Acid.

Free hydrocyanic acid is never found ready formed in nature; a dilute solution of the acid is, however, obtained in the distillation of bitter almonds, and of the stones of peaches, apricots, plums, and quinces, and also of the leaves of the cherry laurel. It is obtained as a concentrated solution when potassium ferrocyanide is distilled with sulphuric acid. Anhydrous hydrocyanic acid forms a clear, very mobile liquid, which solidifies to a crystalline mass at  $-15^{\circ}$  and boils at  $26^{\circ}$ . According to Gay-Lussac, the anhydrous acid has a sp. gr. of 0.6969; it is miscible with water in all proportions, and is extremely poisonous. A dilute aqueous solution forms an official preparation of the British Pharmacopoeia, *Acidum hydrocyanicum dilutum*; it should contain 2 per cent. by weight of hydrocyanide acid, and have a sp. gr. of 0.997.

Hydrocyanic acid in aqueous solution may be estimated either gravimetrically (p. 546) or volumetrically.

In Liebig's volumetric method, 10 to 15 c.c. of the solution to be tested are measured off with a pipette, 5 c.c. of normal sodium hydroxide solution, followed by 0.5 g. sodium bicarbonate added, and after diluting the whole to from 50 to 60 c.c.,  $N/10$  silver nitrate solution run in from a burette, with continual stirring so long as the precipitate formed dissolves in the solution. The titration is finished as soon as a permanent opalescence is formed. The volume of solution taken for titration should not contain more than 0.10 g. HCN. One c.c.  $N/10$  silver nitrate solution = 0.005404 g. HCN.

In the Fordos and Gélis method a quantity of solution containing not more than 0.05 g. HCN is measured off, treated with 4 c.c. of normal sodium hydroxide solution and 0.5 g. sodium bicarbonate, and diluted to about 1000 c.c.; standard iodine solution is then added from a burette until the solution acquires a permanent yellow tinge. One c.c.  $N/10$  iodine solution corresponds to 0.001351 g. HCN. Starch solution should not be employed as an indicator, since its presence leads to low results.

### Cherry Laurel and Bitter Almond Waters.

The hydrocyanic acid in cherry laurel water and in bitter almond water is present partly in the free state and partly in combination with benzaldehyde.

For the estimation of the total cyanogen Feldhaus<sup>1</sup> recommends

<sup>1</sup> *Z. anal. Chem.*, 1864, 3, 34.

the gravimetric method, employing 100 c.c. of the solution and adding to this 1.2 g. of silver nitrate, dissolved in the necessary quantity of water, to which 2 to 3 c.c. of ammonia solution of sp. gr. 0.96 have been added. After the addition of the silver nitrate, the solution is acidified immediately by means of nitric acid. The precipitated silver cyanide is then estimated in the usual way.

The official preparations of the British Pharmacopœia, *Aqua laurocerasi* (cherry laurel water) and *Aqua amygdalæ Amara* (bitter almond water) are tested by titration with silver nitrate in faintly alkaline solution; they should contain 0.1 per cent. of hydrocyanic acid.

According to the German Pharmacopœia, the cyanogen content in bitter almond water is determined volumetrically by diluting 25 c.c. with 100 c.c. of water; 1 c.c. of potassium hydroxide solution and a trace of sodium chloride are added, and the whole titrated, under constant agitation, with *N*/10 silver nitrate solution until a permanent opalescence is formed. The quantity of silver nitrate solution required should not be less than 4.5 c.c., nor more than 4.8 c.c.

### Potassium Cyanide.

Potassium cyanide was formerly manufactured exclusively from potassium ferrocyanide, either by fusing this salt alone, or with addition of potassium carbonate as recommended by Liebig, of sodium carbonate as proposed by Wagner, or finally, with metallic sodium, according to the Erlenmeyer process. Recently the following processes have been introduced. The Reichardt and Bueb process, in which the nitrogen compounds in the gases obtained from the distillation of the vinasses of the beetroot-sugar industry are converted into hydrocyanic acid and ammonia, and the former worked up for cyanide; the Raschen process,<sup>1</sup> worked by the United Alkali Company, in which a solution of a thiocyanate is oxidised by nitric acid and the liberated hydrocyanic acid absorbed in alkali, and the synthetic processes of Siepermann and of Beilby, in which ammonia is caused to react with potassium or sodium carbonate and charcoal. So far, synthetic processes involving the conversion of atmospheric nitrogen into cyanogen have not been commercially successful. Processes in which sodium compounds are employed naturally lead to products which contain a proportional percentage of sodium, whilst in the more recent process of Frank and Caro the fixation of nitrogen by calcium carbide results in the formation of calcium cyanamide  $\text{CaCN}_2$ .

The raw materials used for the manufacture of cyanides, viz.:—Potassium ferrocyanide, sodium ferrocyanide, potassium carbonate, sodium carbonate, ammonia, and metallic sodium, should be as pure as possible, and quite free from sulphur compounds.

<sup>1</sup> *J. Soc. Chem. Ind.*, 1899, 18, 432.

Ferrocyanides are estimated by De Haën's method (p. 561), and the alkalis by titration with acid; the examination for sulphates is made in the usual manner.

Pure, fused potassium cyanide forms a white mass, showing a coarsely or finely crystalline grain, according to the method of cooling adopted in its preparation. It can be obtained in the form of octahedral crystals by evaporating a concentrated solution of the salt; the crystals dissolve readily in two parts of water; in aqueous alcohol, only in proportion to the amount of water present. Commercial potassium cyanide varies in strength to a very marked degree, from 100 down to 30 per cent. In addition to potassium cyanide, it frequently contains sodium cyanide, alkali carbonate, caustic alkali, alkali cyanate, and chloride, and occasionally small amounts of alkali sulphide. Any sodium cyanide present is, in commercial practice, calculated as potassium cyanide, that is, forty-nine parts of sodium cyanide are returned as sixty-five parts of potassium cyanide. In this way the percentage of potassium cyanide in an alkali cyanide may appear higher than it actually is, and a commercial cyanide may contain so much cyanogen that when calculated to potassium cyanide the percentage considerably exceeds 100. In the case of 98 to 100 per cent. cyanide it is therefore advisable to state the value in terms of the contained cyanogen. Cyanides are largely used in gold extraction, electroplating, photography, and also, in America, for the destruction of insect pests.

#### Estimation of Cyanogen by Liebig's Method.

Alkali sulphides, if present, must first be removed by agitating the solution of the cyanide with hydrated bismuth oxide (obtained by treating basic bismuth nitrate with sodium hydroxide, and washing), or by means of freshly precipitated lead carbonate or lead sulphate. The presence of even a small quantity of sulphide is shown by the appearance of a yellow to brown coloration during titration. The presence of free ammonia retards the appearance of the turbidity in the titration, and thus leads to incorrect results; this effect may be overcome by the addition of a sufficient quantity of carbonic acid water. The addition of sodium hydroxide before titration is not permissible, since its presence also retards the end-reaction, and the results obtained may be too high. On the other hand, the addition of a few drops of ammoniacal potassium iodide solution is to be recommended, since it renders the recognition of the end-point much easier, especially in the presence of a large proportion of sodium salts.

For the estimation of total cyanogen, or of potassium cyanide, 5 g. of the cyanide are dissolved in water and the solution made up to 500 c.c.; 50 c.c. of this solution, corresponding to 0.5 g. cyanide, are diluted with an equal volume of water and titrated with  $N/10$  silver

nitrate solution, as described above. One c.c.  $N/10$  silver nitrate = 0.01303 g. KCN.

Should it be necessary to make a complete analysis for potassium and sodium cyanides, cyanates, carbonates, caustic alkali, cyanamide compounds, chlorides, and ferrocyanides, and also for small quantities of alkali sulphides, 50 c.c. of the solution, prepared as above, are treated in a porcelain dish with 5 c.c. of pure, dilute hydrochloric acid of sp. gr. 1.124, and the whole evaporated to complete dryness on the water-bath, due precautions being observed whilst the poisonous hydrocyanic acid is coming off. The potassium and sodium, which are then present as chlorides in the residue, are estimated in the usual manner.

A further 50 c.c. is treated in a stoppered flask, with a slight excess of barium or calcium nitrate, for the estimation of the alkali carbonates. When the resulting precipitate of barium carbonate has settled out, the solution is filtered, and the precipitate washed, air being excluded as far as possible. The carbon dioxide present is calculated from the quantity of barium carbonate obtained. Various methods have been suggested for the estimation of the free alkali hydroxide. The proposal to add magnesium nitrate to the solution, freed from carbonate as above, and then to estimate the precipitated magnesia, does not give reliable results. In Clennel's<sup>1</sup> method the solution is first titrated with silver nitrate solution until opalescence occurs, whereby the hydrocyanic acid is fixed, and then with  $N/10$  acid, using phenolphthalein as indicator. An alternative method is to fix the whole of the cyanide as silver cyanide before titrating with acid, by first adding an equivalent quantity of silver nitrate solution to that required to produce the opalescence. According to Freudenberg, the best results are obtained by employing the method worked out by A. Schlaud in the laboratory of the Deutsche Gold- und Silber-scheideanstalt. In this method, the quantity of alkali hydroxide present is estimated directly by means of a standard neutral solution of Prussian blue, in suspension. The solution is first treated with a moderately strong solution of silver nitrate (about 30 per cent.), until a permanent turbidity is obtained, and a solution of barium nitrate added to precipitate all the carbonate present. The solution is then warmed to 30° to 40° without filtering, and the suspended Prussian blue run in slowly from a burette; the solution must be thoroughly shaken during this addition, which is continued until the "blue" ceases to be split up into ferrocyanide and ferric oxide. This point is recognised by the clear solution above the precipitate acquiring a bluish tinge; the end-point is extremely sharp. Should alkali cyanate be present, care must be taken that the temperature of the solution does not exceed 50°, since above this temperature cyanate

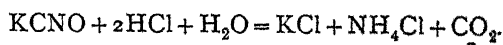
<sup>1</sup> *Eng. and Mining J.*, 1903, 75, 968.



is decomposed with the formation of ammonia and alkali carbonate, which react with the "blue" and so vitiate the results.

The standard solution of Prussian blue is prepared by adding ferric chloride solution to a well-stirred solution of potassium ferrocyanide, taking care that an excess of the latter is always present. The precipitated "blue" is washed repeatedly by decantation until a point is reached at which it ceases to settle well. The solution is then thoroughly shaken to bring the precipitate into suspension, and its strength estimated by means of normal sodium hydroxide solution, after which it is diluted until the strength is such that 10 c.c. of the suspended "blue" correspond approximately to 10 c.c. of *N*/10 sodium hydroxide solution. The Prussian blue solution, which keeps well, should be well shaken before use.

Cyanates are determined by adding a slight excess of neutral silver nitrate solution to the cyanide solution previously freed from alkali hydroxide and carbonate, and allowing the precipitate to settle. The precipitate, which consists, or may consist, of silver cyanide, silver cyanate, and silver chloride, is filtered off, well washed, and then transferred to a beaker or flask, in which it is thoroughly shaken with about 200 c.c. of water, made acid by the addition of 10 c.c. of dilute nitric acid of sp. gr. 1.20, and then digested for an hour on the water-bath; the contents are shaken repeatedly, and the beaker or flask kept covered. By this treatment the silver cyanate goes into solution whilst the other silver salts remain undissolved. The quantity of cyanate is then arrived at by estimating the silver present in the solution, either by weighing as silver chloride, or volumetrically by Volhard's method. To ensure accurate results, the details given above must be closely observed. The following method, due to Herting,<sup>1</sup> is preferable; it depends upon the fact that whereas hydrochloric or sulphuric acid decompose potassium cyanide with complete elimination of the nitrogen as hydrocyanic acid, in the case of the cyanate the nitrogen is quantitatively converted into ammonia, according to the equation:—



0.2 to 0.5 g. of the sample are dissolved in a few c.c. of water in a porcelain dish, dilute hydrochloric or sulphuric acid added, and the whole evaporated to dryness on the water-bath. The residue is dissolved in water, and the nitrogen content estimated by distilling the solution with sodium hydroxide, collecting the distillate in *N*/5 sulphuric acid, and titrating back the excess of acid with *N*/5 ammonia solution. The nitrogen obtained is calculated to cyanic acid or to potassium cyanate; 1 c.c. *N*/5 sulphuric acid = 0.0162 g. KCNO and 0.0086 g. HCNO. Care must, of course, be taken that no ammonium chloride is

<sup>1</sup> *Z. angew. Chem.*, 1901, 14, 585; *J. Soc. Chem. Ind.*, 1901, 20, 838.

present. Milbauer<sup>1</sup> has modified this method by decomposing the cyanate by means of acid potassium sulphate; this allows of the simultaneous isolation of the hydrocyanic acid contained in the cyanide. To separate the resulting silver cyanide from the silver chloride, the mixed precipitate is digested with a solution of mercuric oxide in acetic acid, by which treatment the silver cyanide goes into solution whilst the silver chloride remains undissolved. Or, the hydrocyanic acid may be liberated by distilling the original solution of the cyanide with acetic acid, and the chloride determined in the above residue.

To estimate the ferrocyanide which may result from the presence of iron when dissolving the fused cyanide, a further 50 c.c. of the solution are treated with 5 c.c. of dilute sulphuric acid, evaporated to dryness, washed into a platinum dish, and heated to fusion. When cold, the fused residue is dissolved in water, treated with zinc to reduce the ferric sulphate, and the resulting ferrous salt titrated with permanganate solution. A blank test with similar quantities of sulphuric acid and zinc must always be made, and any permanganate solution consumed in this deducted from that required in the analysis of the sample.

It is further necessary to test the finished product for sodium cyanamide,  $\text{Na}_2\text{CN}_2$ , which compound may be formed as an intermediate product in some of the newer processes of manufacture. It may be detected by adding an excess of a strongly ammoniacal 6 per cent. silver nitrate solution to the diluted solution of the cyanide; a yellow precipitate of silver cyanamide will result, even if only traces of alkali cyanamide are present. Should the solution be free from cyanamide, either no precipitate is formed, or there results, if the solution be sufficiently concentrated, a pure white, shining, crystalline precipitate of ammonium silver cyanide. For the quantitative estimation of cyanamide the solution, freed as above from alkali carbonates and hydroxides, is treated with 6 per cent. ammoniacal silver nitrate solution, the resulting precipitate filtered off, washed, and then heated on the water-bath with dilute nitric acid, shaking at intervals. By this treatment the whole of the silver cyanamide is dissolved. The resulting solution is filtered, and the silver in the filtrate and washings titrated, employing potassium thiocyanate as indicator; the silver thus found is calculated to cyanamide.

Kühling<sup>2</sup> states that the results obtained by this method are inaccurate owing to silver cyanamide being somewhat soluble in dilute ammonia solution, and also because the content of silver does not correspond exactly to the formula  $\text{Ag}_2\text{CN}_2$ . He has accordingly modified the method as follows:—The precipitated silver cyanamide is first washed with a dilute ammoniacal solution of silver nitrate until the filtrate gives no reaction with nitric acid, and then with water until it gives no

opalescence with hydrochloric acid; the precipitate and filter paper are dried in an evacuated exsiccator over sulphuric acid for twelve hours, and the nitrogen in the silver cyanamide determined by the Kjeldahl-Förster method, by heating with phenol-sulphuric acid, sodium thiosulphate, and mercury, and estimating the evolved ammonia volumetrically.

#### The Fordos and Gélis Method for the Estimation of Cyanogen.

The analysis is made on 0.05 g. of the sample, or 5 c.c. of the above solution. The cyanide is dissolved, the solution diluted with water to about 400 c.c., and  $N/10$  iodine solution added from the burette until the solution acquires a permanent yellow tinge. As stated above, the use of starch solution is not permissible. Any alkali hydroxide or free ammonia present in the liquors must be neutralised by the addition of carbonic acid water; in the case of alkali hydroxide alone, an addition of sodium bicarbonate will suffice. Ammonium salts are without influence on the reaction. One c.c.  $N/10$  iodine solution corresponds to 0.003258 KCN.

Under the above conditions of dilution the method gives accurate results. Schnell, who has investigated the method, obtained values varying between 99.5 and 100.1 per cent., as compared with the 100 per cent. obtained by Liebig's method.

#### Sodium Cyanide.

Pure, fused sodium cyanide forms a white mass similar in appearance to potassium cyanide. It crystallises from its aqueous solution with two equivalents of water, in the form of plates; at temperatures above  $33^{\circ}$ , however, it separates in the anhydrous condition, in which state it melts at about  $500^{\circ}$ . Sodium cyanide is prepared by Castner's process, by the interaction of ammonia, sodium, and charcoal, and by Raschen's process (*cf.* p. 549). The commercial product tests as a rule 125 per cent., calculated as potassium cyanide; sometimes, however, products testing as high as 128 per cent. are found on the market. The method of estimating sodium cyanide and its accompanying impurities is the same as that already described under the potassium salt.

#### Ammonium Cyanide.

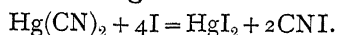
This salt forms colourless cubes, which volatilise with dissociation at  $36^{\circ}$ . It dissolves readily in water and in alcohol; the solutions have an alkaline reaction and an ammoniacal odour, and yield a brown deposit on standing. The salt is very seldom found on the market. Its cyanogen content may be determined either gravimetrically or volumetrically; in the latter case, carbonic acid water must be added in excess before titrating.

### The Cyanides of the Alkaline Earths.

According to Langbein, the cyanides of the alkaline earths are employed in electroplating. For analysis, their aqueous solution is treated with sodium carbonate solution, in the case of the magnesium compound with alkaline carbonate and hydroxide, to precipitate the alkaline earth, the solution filtered, and the cyanogen estimated in the filtrate, in the manner described under potassium cyanide.

### Mercuric Cyanide.

Mercuric cyanide forms colourless quadratic prisms, readily soluble in water; it is used in medicine and in an official preparation in several pharmacopœias. The contained cyanogen may be determined by titrating with iodine solution according to the method of Fordos and Gélis:



For the determination about 0.1 g. of the sample is dissolved in about 400 c.c. of water, and the solution titrated with *N*/10 iodine solution. Should a separation of red or yellow mercury iodide occur during the titration, sufficient potassium iodide must be added to bring the whole of the precipitate into solution. The formation of such a precipitate indicates that more mercury is present than corresponds to the formula  $\text{Hg}(\text{CN})_2$ . Very accurate results are obtainable by this method; experiments have shown that values varying between 99.7 and 99.9 are obtained for every 100 parts of mercuric cyanide present.

## II. DOUBLE CYANIDES

### I. POTASSIUM FERROCYANIDE; YELLOW PRUSSATE OF POTASH

Potassium ferrocyanide was formerly manufactured by heating together potassium carbonate and dried or carbonised nitrogenous materials such as waste leather, horn, wool, or dried blood. This method has now been almost completely replaced by the various processes employed for extracting the cyanogen compounds contained in the "spent oxide" of gasworks, and the analytical methods to be described will accordingly be restricted to these processes. The raw materials involved are:—spent oxide, potassium carbonate, and potassium chloride.<sup>1</sup>

### Examination of "Spent Oxide."

The ordinary spent oxide from gasworks contains from 3 to 16 per cent. of Prussian blue, calculated as anhydrous ferrocyanide of iron

<sup>1</sup> For the analysis of Potassium carbonate and of Potassium chloride, *cf.* pp. 533 and 543.

$\text{Fe}_7(\text{CN})_{18}$ , 0.5 to 3.0 per cent. of ammonium sulphate, and 30 to 50 per cent. of sulphur. The remainder consists of 10 to 30 per cent. of water ferric hydroxide admixed with organic matter, sand, clay, lime, and sodium salts. The spent mixture will also contain tarry matters as an impurity if the gases are insufficiently scrubbed before entering the purifiers.

Particular attention must be paid to the taking of the sample (*cf.* p. 7), since, as a rule, each sample represents a wagon-load of the material. Sampling is best done during loading or unloading, by taking a spadeful from each basket, box, or other receptacle employed, thoroughly mixing the portions withdrawn, spreading out and dividing down in the usual way until about 1 kilo remains. Should the mass be sufficiently dry, the whole is passed through a sieve of about 64 meshes to the sq. cm.

*Determination of Moisture.* Fifty g. of the sample are heated for four hours at  $70^\circ$  in an air-bath. If the material is very damp, it is as a rule difficult to lixiviate. A very dry product, with 10 per cent. or less of water, indicates decomposition; this occurs very readily, owing to the heating which is set up when the mass is stored for any length of time, and which brings about destruction of the thiocyanogen and cyanogen compounds with the formation of ammonium sulphate, and may even cause the mass to fire.

*Determination of Prussian Blue.* The dried material from the moisture determination is finely ground and passed through a sieve of 200 meshes to the sq. cm. Particles of wood or other material remaining on the sieve are further broken up, added to the sieved portion, and the whole carefully mixed. Recently, wet methods of recovery have come into somewhat extended use, such as those of Knublauch, Foulis, and Bueb, in which the hydrocyanic acid in the gas is absorbed in a "standard" scrubber by means of a concentrated solution of ferrous chloride or of ferrous sulphate, with the formation of an insoluble double compound of iron and ammonium ferrocyanides. This double salt in the form of pressed cake contains up to 50 per cent. of "blue," and is almost free from sulphur and thiocyanates. The Chemische Fabrik "Residua" gives the following rules for sampling this material:—In the case of a cyanide mud or slime loaded in a tank-wagon, the contents of the tank are well agitated and three sample bottles taken. Should the product be despatched in small iron drums, which are also employed for 10-ton consignments, the contents of each drum are thoroughly stirred, and approximately equal volumes of the mud drawn from each; the individual samples are then mixed, and three sample bottles, as above, are filled with the mixture. In the case of a pressed mud, the sampling is done by taking about 1 lb. of the cake from each sack, as it is filled at the time of loading.

so taken are thoroughly mixed, and from the average sample so obtained three equal quantities, each of about 2 lbs., are taken, and stored in air-tight, glass bottles.

The determination of the "blue" present in the mixture may be carried out in several ways.

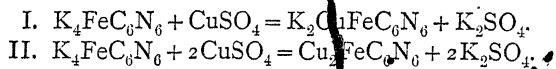
1. *Knublauch's*<sup>1</sup> *Method*. Ten g. of the sample, prepared as above, are treated in a 250 c.c. flask with 50 c.c. of a 10 per cent. potassium hydroxide solution, and allowed to stand, with repeated shaking, for sixteen hours at the ordinary temperature. The flask is then filled to the mark, and after the addition of about 5 c.c. of water the whole is shaken and filtered. Should potassium sulphide be present, the solution must be treated with 1 to 2 g. of lead carbonate before filtering. One hundred c.c. of the filtrate are then added to 25 c.c. of a 6 per cent. ferric chloride solution previously warmed to 60° to 80°, and the mixture heated over a wire gauze and well stirred for several minutes. The solution, which is kept warm, is filtered as rapidly as possible, and the precipitate washed once or twice with hot water to remove any thiocyanate of iron. The filter paper and precipitate are returned to the beaker, 20 c.c. of 10 per cent. potassium hydroxide solution added, and the lumps broken down by pressing them with a glass rod against the sides of the beaker; a little water is then added, and the whole mixed to a uniform cream. The contents of the beaker are washed into a 250 c.c. flask, diluted to this volume, and filtered. One hundred c.c. of the filtrate are transferred to a porcelain dish, 3 c.c. of a 30 per cent. sulphuric acid solution added, and the acidified solution titrated with copper sulphate solution. The end-point is determined by spotting a drop of the liquid and a drop of a solution of a ferrous salt at a slight distance apart on a piece of Schleicher and Schüll's spotting paper. Should the precipitation of the ferrocyanide as the copper salt not be complete, a coloration will appear at the line of contact formed by the spreading of the drops. The intensity of the stain and the time taken for its development vary according to the quantity of ferrocyanide still remaining in solution (*cf.* p. 427), and thus affords a guide to the course of the titration.

The copper sulphate solution is prepared by dissolving 12.5 g. of pure crystallised copper sulphate in water, and making up to 1 litre. It is standardised against a second solution, containing 4 g. of pure potassium ferrocyanide to the litre, by adding 100 c.c. of this solution to 25 c.c. of hot, 6 per cent. ferric chloride solution, and treating the resulting precipitate exactly as above. The titre of the copper solution follows on dividing 0.4 by the mean number of c.c. obtained as an average of four concordant titrations.

It is absolutely essential that uniform conditions be observed both

<sup>1</sup> *Jo Gasbeleucht.*, 1869, 35, 450; *J. Soc. Chem. Ind.*, 1889, 8, 732.

in standardising the solution and in estimating the "blue," more particularly as regards the quantities of potassium hydroxide and of sulphuric acid employed; otherwise it is impossible to be certain that the copper ferrocyanide precipitate has always the same composition. The reaction is not altogether uniform; it proceeds in part according to equation I. and in part according to equation II. :—



The method finds considerable application in technical work, but some experience is necessary in the determination of the end-point of the titration.

J. M. Popplewell<sup>1</sup> recommends a modification of Knublauch's method whereby the analysis may be completed in one and a half hours.

2. *Zulkowsky's modified Method.* This method has been adopted by the Chemische Fabrik "Residua," and is carried out by them as follows :—

Fifty g. of the thoroughly mixed cyanogen mud, or 90 g. of the pressed cake, are boiled with 50 c.c., or, in the case of the cake, with 100 c.c. of potassium hydroxide solution of sp. gr. 1.25 and about 200 c.c. of distilled water until all ammonia has been driven off; the solution is then diluted to 1010 c.c. (10 c.c.=correction for volume of insoluble matter). The contents of the flask are well shaken, filtered through a dry, pleated filter paper, and 25 c.c. of the filtrate, after dilution with 50 c.c. of water and 10 c.c. of dilute sulphuric acid (100 parts acid of 1.84 sp. gr. to 1 litre), titrated with standard zinc sulphate solution. In commercial dealings the difference between the buyer's and seller's analyses should not exceed  $\frac{1}{2}$  per cent. The zinc sulphate solution is prepared by acidifying 10.2 g. of pure zinc sulphate ( $\text{ZnSO}_4 + 7\text{H}_2\text{O}$ ) with 10 c.c. of sulphuric acid of sp. gr. 1.67, and dissolving in water to 1000 c.c.; the addition of the acid improves the keeping qualities of the solution. The zinc sulphate solution is standardised against a freshly prepared solution of potassium ferrocyanide containing 10 g. of crystallised ferrocyanide to the litre. For the titration, 25 c.c. of the ferrocyanide solution diluted with 50 c.c. of distilled water and 10 c.c. of dilute sulphuric acid (sp. gr. 1.67) are taken, and the end-reaction judged by spotting, using Schleicher and Schüll's spotting paper, No. 601, with a ferric solution (containing iron equivalent to 1 per cent. ferric oxide) as indicator.

3. *Nauss' Method.* This is a modification of Knublauch's method, in which the use of the spotting test is obviated. Ten g. of the

material are treated with 50 c.c. of a 10 per cent. sodium hydroxide solution in a 500 c.c. flask, the mixture shaken repeatedly, and allowed to stand for some time at atmospheric temperature until the "blue" has been completely decomposed. According to Knublauch, this decomposition requires fifteen hours. The use of the dilute alkali solution is intended to prevent the formation of alkaline sulphides. The flask is filled to the mark, a further 5 c.c. of water added to allow for the volume occupied by the solid matter present, and after thorough mixing, an aliquot portion is filtered off. It is advisable not to take a greater volume of solution than corresponds exactly to from 1 to 2 g. of the material. This volume, say 50 c.c., is allowed to flow into 10 to 15 c.c. of a hot solution of iron alum (200 g. + 100 g. sulphuric acid in the litre) to convert the sodium ferrocyanide into Prussian blue, and the mixture heated on the water-bath until the characteristic sweet smell, which is probably due to the decomposition of soluble non-blue-forming cyanogen compounds, has disappeared. The mixture is filtered hot through a pleated filter paper, kept warm in a water-jacketed funnel, and the insoluble matter washed with hot water until the washings are quite free from sulphuric acid. The filter paper and precipitate are then transferred to a flask, a little water added, and the whole heated to boiling, with frequent agitation, to separate the filter paper and precipitate as completely as possible; the "blue" is then estimated directly by means of sodium hydroxide solution. This is done by adding  $N/50$  sodium hydroxide solution in successive small quantities until all the "blue" has been decomposed; the decomposition takes place readily on warming for a short time. The excess of alkali is then titrated back by the gradual addition of  $N/50$  acid, the solution being maintained hot and shaken continuously. The titration is finished as soon as the solution acquires a permanent yellowish green coloration. It is absolutely essential to heat the solution, otherwise the green coloration due to the reformation of "blue" appears in a short time even in the presence of alkali.

This method may be extended to the determination of cyanogen in coal gas. The results obtained agree well with those of the Drehschmidt-Burschell method (cf. p. 560).

According to Bernheimer and Schiff,<sup>1</sup> the results obtained by direct titration, according to Knublauch's method, are lower than those obtained by igniting the reprecipitated "blue" and weighing the resulting ferric oxide.

Their experimental results have been confirmed by Lührig,<sup>2</sup> who also obtained higher figures both by the Nauss and by the Leybold-Moldenhauer (cf. *infra*) methods than by that of Knublauch. According to Lührig, none of these methods can be regarded as absolutely reliable;

<sup>1</sup> *Chem. Zeit.*, 1902, 26, 227.

<sup>2</sup> *Ibid.*, 1939.



at present it is therefore advisable for buyer and seller to agree to the adoption of one and the same analytical method in their dealings.

4. *Moldenhauer and Leybold's Method.* The "blue" is decomposed by sodium hydroxide solution, the resulting sodium ferrocyanide evaporated with sulphuric acid, and the solution finally heated until the ferrocyanide has been decomposed. The sulphate of iron formed is then reduced to the ferrous condition by zinc and sulphuric acid, and the solution titrated with potassium permanganate.

According to Auerbach,<sup>1</sup> the results obtained by this method are too high because the alkali extracts, in many cases, other iron compounds present in the mass, in addition to the ferrocyanide.

5. *Drehschmidt's Method.*<sup>2</sup> Ten g. of the mass are treated in a 500 c.c. flask with about 150 c.c. of water and 1 g. of ammonium sulphate; 15 g. of mercuric oxide are then added, and the mixture heated to boiling and maintained at boiling temperature for a quarter of an hour. The solution is allowed to cool, and  $\frac{1}{2}$  to 1 c.c. of a saturated mercurous nitrate solution added together with sufficient ammonia to produce complete precipitation, the whole being well agitated so as to precipitate any thiocyanic acid and hydrochloric acid present in the solution. The flask is then filled to the mark and a further 8 c.c. of water added, to allow for the volume occupied by the precipitate; the whole is then mixed, and filtered through a dry filter paper. Two hundred c.c. of the filtrate, corresponding to 4 g. of the sample, are transferred to a 400 c.c. flask, and ammonia solution (at least 6 c.c. of 0.91 sp. gr.) and 7 g. of zinc dust added, to separate the mercury from the mercuric cyanide and convert all the cyanogen into ammonium cyanide; the mixture is then shaken for several minutes, 2 c.c. of a 30 per cent. sodium hydroxide solution added to prevent volatilisation of hydrocyanic acid, the volume made to 400 c.c., and the mixture again filtered through a dry filter paper. One hundred c.c. of the filtrate, corresponding to 1 g. of the sample, are added to an excess of  $N/10$  silver nitrate solution (30-35 c.c. will generally suffice) in a 400 c.c. flask, the mixture shaken and acidified with dilute nitric acid, whereby the cyanogen is obtained as silver cyanide. The acidified solution is shaken to facilitate the settling of the precipitate, the flask filled to the mark with water, again shaken, and the contents filtered through a dry filter paper. The excess of silver is then estimated by titrating 200 c.c. of the filtrate with  $N/20$  ammonium thiocyanate solution, according to Volhard's method. The quantity of the latter solution required gives the excess of silver, and is to be deducted from the volume of silver nitrate solution taken.

According to Burschell,<sup>3</sup> thiocyanate cannot be completely removed

<sup>1</sup> *J. Gasbeleucht.*, 1896, 39, 258.

<sup>2</sup> *Ibid.*, 1892, 35, 221 and 268.

<sup>3</sup> *Ibid.*, 1893, 36, 8; *J. Soc. Chem. Ind.*, 1894, 13, 138.

from the solution by means of mercurous nitrate. For this reason he recommends first extracting the "blue" with alkali hydroxide, as in Knublauch's method, then reprecipitating by addition of an iron salt, and decomposing this purified "blue" by mercuric oxide. The cyanogen is then estimated as silver cyanide by Drehschmidt's method.

Lubberger<sup>1</sup> also recommends the employment of the purified "blue," and not the original spent oxide, for decomposition with mercuric oxide, since the latter may contain, in addition to ferrocyanide, other cyanogen compounds which will neither yield "blue" nor give a precipitate with iron salts, but which will nevertheless pass into solution on boiling with mercuric oxide, and thus be calculated to ferrocyanide. He maintains that, coupled with extraction by alkali, the Drehschmidt method affords the most trustworthy and accurate results. That the modification greatly affects the results obtained, has been shown by Lubberger, who, in examining nine different samples of spent oxide by the original and modified methods, obtained results showing differences varying between 1.7 and 3.2 per cent.

The manufacture of potassium ferrocyanide from spent oxide is carried out at the Kunheim works, Berlin,<sup>2</sup> in the following manner:—The material is first lixiviated with warm water to extract the soluble ammonium salts, including ammonium thiocyanate and ammonium sulphate, which are recovered from the solution so obtained. The residue is mixed with caustic lime and heated with steam, to convert the insoluble cyanide of iron into the soluble calcium ferrocyanide, ferric hydroxide being separated at the same time. The calcium ferrocyanide is extracted with water, and the residue, which is rich in sulphur, is utilised for the manufacture of sulphuric acid by burning, in the usual manner. The calcium ferrocyanide solution is concentrated and potassium chloride added to the boiling solution, whereby the insoluble potassium calcium ferrocyanide,  $K_2CaFeC_6N_6$ , is precipitated. This precipitate is washed and heated with potassium carbonate solution when calcium carbonate and potassium ferrocyanide are formed; the latter salt is obtained in the crystalline form on evaporating the solution.

The intermediate product, potassium calcium ferrocyanide, sometimes appears on the market. For its analysis, 1 g. is boiled with sodium carbonate solution containing 0.5 g. of the carbonate, and the resulting ferrocyanide solution filtered from the calcium carbonate produced. The filtrate is then titrated with potassium permanganate solution according to De Haën's<sup>3</sup> method, by diluting to about 1000 c.c., acidifying with sulphuric acid, and adding permanganate solution until a permanent red coloration results. A permanganate solution corre-

<sup>1</sup> *J. Gasbeleucht.*, 1898, 41, 124; *J. Soc. Chem. Ind.*, 1898, 17, 182.

<sup>2</sup> Kunheim and Zimmermann, Ger. Pat. 26884.

<sup>3</sup> *Annalen*, 1854, 90, 160.

sponding to 0.005 g. Fe per 1 c.c. represents 0.0295 g.  $K_2CaFeC_6N_6$ ; that is, 1 g. Fe = 5.895 g. of the double salt.

Should there be any risk of the treatment with alkali dissolving substances capable of reacting with permanganate; it is necessary to acidify the alkaline extracts with sulphuric acid, then to evaporate, and finally to heat the mixture in a platinum dish until fumes of sulphuric acid begin to come off; the iron in the residue is then determined by means of permanganate, as described under the Moldenhauer-Leybold method (cf. *ante*). If preferred, the iron may be precipitated by addition of ammonia and weighed as oxide, instead of titrating with permanganate.

Conroy<sup>1</sup> has found De Haën's method unsatisfactory except in the case of pure ferrocyanides. With commercial products, errors are introduced, partly by sulphides extracted by the action of the alkali, hydroxide on the mixed cyanide and sulphide of iron, and partly by thiocyanate, which is almost always present in spent oxide. Since 1 c.c. of  $N/10$  potassium permanganate solution requires for its reduction 0.0422 g. of crystallised potassium ferrocyanide, whilst it only requires 0.001616 g. of potassium thiocyanate, 1 per cent. of the latter requires as much permanganate solution as more than 26 per cent. of ferrocyanide. Hence, even traces of thiocyanate remaining in the precipitated "blue," which is very difficult to wash, will greatly vitiate the results. If thiocyanates are present, the "blue" should therefore always be dissolved in alkali, and reprecipitated before titration with permanganate. If ferrocyanides and thiocyanates are present together, Zulkowsky's method (p. 558) is much to be preferred to that of De Haën.

### Commercial Products.

1. *Potassium Ferrocyanide*,  $K_4FeC_6N_6 + 3H_2O$ , also known as yellow prussiate of potash, crystallises in amber or lemon yellow tetragonal prisms.

The ferrocyanide content of the commercial product is determined by De Haën's method. The titre of the permanganate solution for crystallised potassium ferrocyanide is obtained by multiplying the titre for iron by 7.56.

The impurities likely to be present are potassium sulphate, potassium carbonate, and potassium chloride. The first is recognised by the addition of barium chloride to an aqueous solution of the salt previously rendered slightly acid by addition of hydrochloric acid; the presence of potassium carbonate is shown by the frothing on acidification; potassium chloride is detected by boiling the aqueous solution with chlorine-free mercuric oxide, filtering, acidifying the filtrate with nitric acid, and then adding silver nitrate solution.

Potassium ferrocyanide finds extended application in dyeing, and in the manufacture of Prussian blue and of potassium cyanide.

2. *Potassium Ferricyanide*, or red prussiate of potash,  $K_3FeC_6N_6$ , is prepared by oxidising the ferrocyanide either with chlorine, lead peroxide, potassium permanganate, or electrolytically. On evaporation, the solution yields the anhydrous salt in the form of red monoclinic prisms which are readily soluble in water. The solution deepens in colour on exposure to light, and a blue precipitate is formed. The salt is employed in dyeing, and also in the preparation of photographic printing papers.

The cyanogen content is estimated by reducing the salt to ferrocyanide. This reduction is effected by dissolving 2 g. of the salt in 100 c.c. of water, treating with excess of potassium or sodium hydroxide solution, and then adding ferrous sulphate solution, in successive small quantities, until the colour of the precipitate becomes dark owing to the separation of ferrosoferric oxide. The solution is then further diluted to 500 c.c., 250 c.c. = 1 g. substance, filtered off, acidified with sulphuric acid, and the ferrocyanide estimated by De Haën's method.

3. *Sodium Ferrocyanide*, or sodium prussiate,  $Na_4FeC_6N_6 + 10H_2O$ . This salt, which is also a commercial product, crystallises in yellow monoclinic prisms. It is obtained from the calcium ferrocyanide obtained on treating spent oxide with lime, in the manner already described. The calcium is precipitated from this solution as calcium carbonate on treatment with soda ash, and the resulting solution of sodium ferrocyanide concentrated and crystallised. The sodium salt is examined in exactly the same way as the potassium salt. Where the Bueb process is worked, sodium ferrocyanide is obtained directly by treating the "blue" with caustic soda.

Sodium ferrocyanide is also readily prepared from the mixture of sulphide and cyanide of iron obtained in the reduction of thiocyanates by Conroy's process,<sup>1</sup> by heating a solution of a thiocyanate with an iron salt and metallic iron.

In addition to potassium ferrocyanide and sodium ferrocyanide, there are also three double potassium-sodium ferrocyanides with three different ratios between the potassium and sodium present. The examination of these salts offers no difficulties. The ferrocyanide content is determined by De Haën's method, and the potassium and sodium in the usual manner.

## 2. OTHER CYANOGEN DOUBLE SALTS

The method of estimating the cyanogen in double salts is based on the discovery of H. Rose, that precipitated mercuric oxide decomposes

<sup>1</sup> Eng. Pat. 3869, of 1896; *J. Soc. Chem. Ind.*, 1898, 17, 98.

most double cyanides, such as potassium nickel cyanide, potassium zinc cyanide, and the ferro- and ferricyanides, with the formation of oxides of the metals, whilst the whole of the cyanogen is converted into mercuric cyanide. The reaction does not, however, hold good in the case of cobaltcyanides. The estimation is carried out by boiling the double cyanide with water and excess of mercuric oxide for several minutes until decomposition is complete; the solution is then filtered, and the insoluble residue washed with hot water. Should the oxide be precipitated in such condition that it cannot be filtered, alum solution<sup>1</sup> is added, or, if this be not permissible, nitric acid<sup>2</sup> until the alkaline solution is almost neutralised. The cyanogen is then determined by the Fordos and Gélis method (p. 554), after adding the requisite sodium bicarbonate to the filtrate. Should it be necessary to determine the alkali, the filtrate is evaporated to dryness with hydrochloric acid to drive off nitric and hydrocyanic acids, and the alkali and the mercury in the residual chlorides separated in the usual manner. When the alkali is determined, the addition of alum previous to filtration must of course be omitted. In the case of a double cyanide of potassium and zinc, it is unnecessary to separate the zinc oxide previous to determining the cyanogen; the solution is simply treated with sodium bicarbonate and the cyanogen then determined by direct titration with iodine solution.

### III. THIOCYANATES

#### Ammonium Thiocyanate, $\text{NH}_4\text{CNS}$ .

Ammonium thiocyanate is obtained as a by-product in the manufacture of potassium ferrocyanide from spent oxide (*cf.* p. 561); it is also manufactured synthetically from carbon bisulphide and ammonia.

*Raw Materials; Spent Oxide.* The thiocyanate is estimated by adding 50 g. of the spent oxide to 500 c.c. of water contained in a litre flask, and allowing it to digest overnight at the ordinary temperature. After standing, the flask is filled to the mark and a further 30 c.c. of water added, to allow for the volume occupied by the 50 g. of the spent oxide; the whole is then well shaken and filtered. Fifty c.c. of the solution, corresponding to 2.5 g. of the sample, are treated with sufficient barium chloride, heated, and the precipitated barium sulphate filtered off and thoroughly washed. The filtrate and washings are then made strongly acid by addition of nitric acid, and warmed, when, as described by Volhard<sup>3</sup> and later by Alt,<sup>3</sup> the sulphur of the thiocyanate is in a short time oxidised to sulphuric acid, which forms barium sulphate with the excess

<sup>1</sup> *Cf.* Fresenius, *Quantitative Analysis*, 6th edition, 1876, vol. i., pp. 376-7.

<sup>2</sup> *Z. anal. Chem.*, 1879, 18, 282.

<sup>3</sup> *Ibid.*, 1892, 31, 349.

of barium chloride present in the solution. The hydrocyanic acid liberated in the reaction is expelled by boiling, the solution diluted with hot water, and the barium sulphate filtered off and weighed. Each molecule of thiocyanic acid gives 1 molecule of barium sulphate. Working with pure thiocyanates, H. Alt obtained satisfactory results by this method.

The process is not applicable when the solution contains, in addition to thiocyanates and sulphates, other sulphur compounds, which are oxidised to sulphates by nitric acid.

In the presence of sulphites and thiosulphates the thiocyanic acid may be precipitated as white cuprous sulphocyanide,  $\text{Cu}_2(\text{CNS})_2$ , in the following manner:—To 50 c.c. of the solution is added a solution of copper sulphate, containing about 1 g. of crystallised copper sulphate in dilute solution, the whole diluted to about 100 c.c., treated with sulphur dioxide gas, and allowed to stand for some time. The precipitate is allowed to settle at the ordinary temperature, and is then filtered and washed. The dried precipitate and filter ash are mixed with pure ground sulphur, and ignited in a current of hydrogen until the weight is constant. This method gives satisfactory results, generally however somewhat on the low side, owing to the cuprous sulphocyanide not being absolutely insoluble; 1 molecule of cuprous sulphide corresponds to 2 molecules of thiocyanic acid.

Linder<sup>1</sup> has devised a volumetric modification of this method based on the decomposition of cuprous thiocyanate by sodium hydroxide or carbonate, whereby copper oxide and sodium thiocyanate are formed. The solution containing the thiocyanate is treated with sodium sulphite and a distinct excess of copper sulphate, the whole boiled for one to two minutes, filtered, and the precipitate washed three times with boiling water. The precipitate is then washed back into the original flask, decomposed by boiling for two minutes with 25 c.c. of a 3 per cent. solution of sodium carbonate, the solution filtered through the filter paper on which the original precipitate was collected to ensure the solution of any traces of cuprous thiocyanate that may have remained attached, the residue washed three times with boiling water and the filtrate, after cooling, titrated by Volhard's method after the addition of 5 c.c. of nitric acid. If the solution contains more than 0.1 g.  $\text{HCNS}$ , sodium hydroxide must be used for the decomposition in place of sodium carbonate; both reagents must of course be free from chloride. If any ferrocyanide is present, it is first removed by precipitation with iron alum and the thiocyanate estimated in the filtrate.

To separate thiocyanic acid from chlorides, C. Mann<sup>2</sup> recommends the addition of copper sulphate solution to the thiocyanate solution, and

<sup>1</sup> *Annual Report on Alkali, etc., Works*, 1907, p. 39; *J. Soc. Chem. Ind.*, 1907, 26, 683.

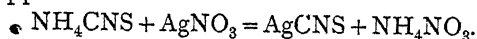
<sup>2</sup> *Z. anal. Chem.*, 1889, 28, 668.

then passing in sulphuretted hydrogen until the resulting precipitate begins to turn brown, at which stage some copper must still be in solution, otherwise more copper sulphate must be added. The solution is filtered and the precipitate washed. The thiocyanic acid is then present in the precipitate as cuprous thiocyanate, whilst the chlorine is in the filtrate, and may be estimated by means of silver nitrate. In two cases in which 0.302 g. and 0.053 g. of ammonium chloride were added to 5 g. of pure ammonium thiocyanate, 0.607 g. and 0.104 g. of silver as silver chloride were obtained respectively, instead of the calculated quantities 0.609 g. and 0.107 g.

According to Volhard,<sup>1</sup> the oxidation of thiocyanic acid by nitric acid may also be applied to the estimation of chlorides in the presence of thiocyanate. In applying this method to the determination of the chlorine, 2 to 3 g. of the thiocyanate are dissolved in 400 to 500 c.c. of water, the solution heated on the water-bath, and nitric acid added, in small quantities at a time, so long as a reaction can be observed. The mixture is allowed to stand on the water-bath, water being added from time to time to replace that lost by evaporation, until a test sample of the solution ceases to give the thiocyanate reaction with a solution of a ferric salt acidified with nitric acid. The solution is then made alkaline by addition of ammonia, transferred to a dish, and evaporated on the water-bath until about one-third of the solution has been driven off. The residual solution will then be free from thiocyanic and hydrocyanic acids, and may be titrated for chlorine with silver nitrate solution in the usual way. It is stated that no appreciable amount of chlorine is evolved during the decomposition of the thiocyanate.

To separate thiocyanic acid from hydrocyanic and hydroferricyanic acids, the hydrocyanic acid is estimated by titration with silver nitrate solution as described on p. 550, the hydroferricyanic acid in a second portion is converted into ferrous sulphate as described on p. 560, and titrated with permanganate, whilst the thiocyanic acid is oxidised, in a third portion, with nitric acid as described above, and the barium sulphate weighed.

Ammonium thiocyanate crystallises in colourless plates, which are deliquescent, readily soluble in alcohol, and melt at 159°. The estimation of the thiocyanate in the pure salt, free from chlorine, is made by Volhard's method,<sup>2</sup> in which a solution, containing about 0.1 g. of thiocyanic acid in 100 c.c., is acidified with nitric acid, a small quantity of iron alum solution (free from chlorine) added, and titrated with *N*/10 silver nitrate solution until the red colour of the ferric thiocyanate completely disappears:—



The ammonia in ammonium thiocyanate cannot be estimated by

<sup>1</sup> *Z. anal. Chem.*, 1879, 18, 282.

<sup>2</sup> *Ibid.*, 1874, 13, 242.

distilling the solution with alkali hydroxide, since this also decomposes the thiocyanic acid with the formation of ammonia. The liberation of the ammonia can, however, be effected by calcined magnesia, which is without action on the thiocyanic radical.

Ammonium thiocyanate forms the starting point for preparation of the other thiocyanates.

#### Potassium Thiocyanate, KCNS.

Potassium thiocyanate is obtained by treating the ammonium salt with potassium carbonate. It forms long, colourless prisms with four-sided pyramidal ends. The salt is readily soluble in water, and deliquesces in the air. The estimation of the thiocyanogen content is carried out exactly as in the case of the ammonium salt.

The thiocyanates are used in dyeing and in calico-printing.

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## CLAY

By P. KREILING, Berlin. English translation revised by W. BURTON, Director of Pilkington's Tile & Pottery Co., Clayton, Lancashire.

CLAY is a decomposition product of aluminous rocks. It consists of varying mixtures of minerals, its characteristic and most valuable constituent being "Clay-substance," *i.e.*, amorphous, hydrated silicate of alumina. The properties of plasticity, setting on drying and complete hardening on burning, are primarily due to this constituent. The extraordinary variety of clays and their diverse properties and applications are determined by variations in the physical properties of the clay-substance, and in the physical state, chemical composition, and amount of the other admixed minerals. From the technical point of view, it is necessary to distinguish between the clay-substance which gives plasticity and other substances which are *aplastic* or which act as fluxes in firing. All substances which lessen the plasticity or working properties of a clay are called shortening, "lean," or aplastic materials. Fluxes are those substances which render a clay more easily fusible. All such substances however act as aplastic materials by diminishing the plasticity of the clay in working; the special properties of the fluxes only become apparent at the higher temperatures of the firing process, and are naturally most pronounced when the substances are in a sufficiently fine state of division. The usual mineral impurities found in clays, which act as fluxes, are the alkalis or alkali silicates, and the oxides of iron, calcium, and magnesium; free silica, in whatever form it may be contained in the clay, also acts as a flux at a sufficiently high temperature. The most refractory clays are accordingly those that approach most nearly to the composition of the most characteristic clay-substance, the pure hydrated silicate of alumina,  $\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2 \cdot 2\text{H}_2\text{O}$ .

In the investigation of the technical qualities of a clay, both mechanical tests and chemical analysis are necessary; under the latter head a distinction must be drawn between a complete quantitative analysis and what is known as a "rational analysis." So far as working properties are concerned, priority must be given to mechanical tests, but to form a complete idea of the behaviour of a clay they must

be supplemented by chemical analysis. The chemical analysis of clays has been directed to two distinct ends: firstly, to determine the composition of pottery clays in relation to the production of fine pottery; and secondly, for purposes of scientific investigation. Zschokke<sup>1</sup> has suggested the adoption of a combined chemico-mechanical analysis based on elutriation and rational analysis; whilst there is nothing to be said against such a method, it is necessary to emphasise the fact that physical tests are the most useful in determining the working properties of a clay; they may be supplemented by chemical analysis when desirable.

## PHYSICAL EXAMINATION

The object of a physical examination is, as stated, to determine the working properties of clays; from the results obtained positive conclusions can be drawn as to the applicability or otherwise of any particular clay for a specific use. The examination includes:—

1. The estimation of the mineral mixtures composing the clay, and their state of division.
2. The determination of the plasticity, or power of fashioning.
3. The behaviour of the clay on drying.
4. The behaviour of the clay during firing, and its refractoriness or otherwise.

### I. ESTIMATION OF THE MINERAL MIXTURES COMPOSING THE CLAY, AND THEIR STATE OF DIVISION

As already stated, clays are mixtures of various minerals of which some form of hydrated silicate of alumina is the most important, all of which are generally in a finely divided state. Usually the "Clay-substance" is the finest of all the constituents of a clay, the sand, mica, and other mineral ingredients being of sensibly coarser grain. This is, however, not invariably the case, *e.g.*, with the white clays frequently found as a decomposition product in mountain limestones, as in that of North Wales and Derbyshire (W. Burton).

For the purpose of separating these various substances, a method of *Elutriation* is used, but this is naturally very incomplete as a scientific method, since it does not effect the decomposition of the clay into its constituents, either in the chemical or in the mineralogical sense. The treatment only effects an approximate separation of the various substances into finer and coarser portions, a matter of the highest importance (especially with regard to the latter), in respect to the working properties of the clay. An exaggerated idea of the value of this

<sup>1</sup> *Baumaterialienkunde*, 1902, Nos. 10 and 21.

process of elutriation has led to the construction of several sensitive and complicated pieces of apparatus, such as the "Elutriation Apparatus" devised by Schöne (*cf.* p. 690).

The actual requirements of practical work are fully met by the use of a series of suitably graded sieves. Sieves of about 12 cm. diameter, formed with brass rims, across which are stretched webs of wire gauze, are the most convenient. The graduation of the sieves to be employed depends on the particular clay and its prospective use, but for most purposes two sieves, one of 900 and the other of 4900 meshes per sq. cm., are sufficient. The coarser sieve is placed in a large funnel supported in the ring of a retort stand, so arranged as to deliver all the material that passes through it on to the finer sieve. Where it is necessary to retain and collect the finest portions of a clay, the second sieve is also supported in a funnel, the delivery tube of which opens over a large glass jar.

The separation is best conducted by placing from 100 to 500 g. of the clay in a glazed jar or porcelain dish, covering it with water, and leaving it to stand until completely softened. The mass is then well stirred into an even state of suspension with a soft brush. The finer portions are poured off first into the coarser sieve, care being taken that any lumps of clay and the coarser sediment remain behind in the mixing vessel. This process of mixing and pouring off is continued until the added water remains almost clear. The residue in the mixing vessel is then washed into the sieve by means of a wash-bottle, and all that is retained by the sieve is repeatedly washed until the water that flows away is quite clear. The mass on the sieve may need gentle stirring (not vigorous rubbing) from time to time, with the brush previously used, to facilitate the passage of the water and of the finer particles. If it is necessary to brush the second fine sieve, a different brush should be used, and, finally, the washings from each brush should be run through the respective sieves. When the washing is completed, the sieves and their contents are dried at a moderate heat, and the contents carefully removed from each sieve and separately weighed on a sufficiently delicate balance. In this way the percentage of the two residues can be readily calculated from the amount of clay taken.

The next step is to form a reasonable idea of the nature of the residues, and to ascertain whether they contain substances that might prove detrimental in practice. The residues are spread out on sheets of white paper and examined with a lens, or for a more thorough examination, with a microscope. Different common minerals may be readily recognised by their appearance, their hardness, or their behaviour under simple chemical tests. The following substances are generally regarded as detrimental, especially if they occur in quantity or in particles of definite size: Calcium carbonate, gypsum, and iron

pyrites, though finely divided calcium carbonate may generally be disregarded. If the colour or whiteness of the fired product is of importance, then gypsum and iron pyrites frequently prove a serious drawback to the use of otherwise suitable clays. A conclusive proof of the detrimental nature of the coarser impurities can be made by mixing the residue with a small quantity of the clay so as to intensify their effect. The size of the granules in the coarse residue is measured along the greatest axis, and is generally stated thus: "Granules range up to  $x$  mm."

## II. PLASTICITY

The exact determination of the plasticity of a clay is very difficult to effect, but as only a practical working guide is usually required, sufficient information can, as a rule, be obtained by an approximate estimation of the amount of water needed to bring a clay into the condition in which it is readily workable without being too soft. Speaking generally, the more plastic a clay is, the more water it will absorb without becoming fluid, so that a plastic clay will give a working mass of lower specific gravity than a less plastic clay. In exceptional cases a clay may contain foreign substances of such a nature or in such amount as to interfere with this test, but when the conditions are reasonably similar, the method affords a rapid means of comparing the plasticity of various clays.

To carry out the determination, a metal or glass ring is taken of such a size that when closed with covering plates at each end it encloses a space of 70 c.c. This ring is placed on a thick sheet of glass, and is filled with the watered clay in its most plastic condition. A steel ruler or spatula is then wetted, drawn over the rim until the surface of the clay is faultlessly level with the mould, the mould then turned over on to another sheet of glass, and the bottom surface of the clay accurately levelled. The metal rim and the sheets of glass should be lightly oiled to facilitate the delivery of the clay (W. Burton). The weight of the mass of clay (of 70 c.c. in bulk) is then determined, and is a good index of the plasticity. If the weight is 120 g. or less, then the clay is highly plastic or "flat"; if from 120 to 125 g., the clay is particularly plastic; if from 125 to 130 g. weight, the plasticity is still marked; clays giving weights of 130 to 135 g. are sufficiently plastic for many purposes, but when the weight rises from 135 to 140 g. the clay is "lean" and deficient in plasticity. The presence of calcium carbonate interferes with this rapid determination more than any other factor; the weight of the mass obtained is then considerably lowered, so that the omission of due allowance for this ingredient may easily lead to deceptive conclusions.

From the indications given by the foregoing method, further infor-

mation may be gained by determining the amount of some definite aplastic substance that can be added to the clay without impairing its working properties or its behaviour on drying and firing. It is to be borne in mind that a very plastic clay is improved in these respects by the addition of "leaner" clays or of aplastic substances; also, that the tenacity of the clay prepared as described above, when air-dried, has been taken as a measure of the plasticity, whereas, in fact, it is only a measure of the binding power. The various properties of plasticity, water-absorption, and binding power merge into each other in such a way that a separate determination of each is hardly possible; nevertheless, the amount of aplastic material, such as fine sand, flint, or grog, which can be properly added to a plastic clay to fit it for use in the factory, is a very important practical factor.

The determination of the tenacity of air-dried clay bodies demands such care and attention, if reliable results are to be obtained, that it is not generally practised in a technical examination.

### III. BEHAVIOUR OF CLAYS ON DRYING

A study of the behaviour of clays on drying includes the measurement of the contraction in drying, and the observation of the phenomena exhibited during the process. To determine the contraction of a clay or clay mixture, small sample blocks, generally  $9 \times 4.5 \times 2$  cm. are carefully moulded in metal or wooden moulds, from the plastic mass. Immediately they are removed from the moulds the blocks are marked and weighed, and then allowed to dry. The linear contraction may be measured in various ways, of which, perhaps, the best is to describe a circle of exactly 5 cm. radius on the block with a sharp-pointed pair of compasses; when the block is completely dry and its contraction finished, the difference in the measurement of its radius multiplied by 20 gives the percentage measure of the linear contraction.

The amount of water added to the clay to bring it to a working condition influences the contraction; this amount is given by the difference in weight between the freshly moulded and the dried block, and it is best expressed as a percentage of the weight of the dried clay. The contraction and the percentage of added water may be expressed as follows: In presence of 20 per cent. of added water, the linear contraction in drying is, say, 10 per cent.

It is further important to observe whether the moulded and dried samples are free from cracks, and whether the edges and sides remain sound and complete. Faults in these respects are generally due to over-plasticity, and can be remedied by the suitable addition of shortening material. The dried samples must, of course, be sufficiently tenacious to stand the necessary handling for their further treatment.

## IV. BEHAVIOUR OF CLAYS ON FIRING

For a rapid examination of the behaviour of a clay when fired, it is usual to employ a small furnace, preferably heated by gas, such as an ordinary muffle or an experimental gas furnace. The dried sample blocks are fired at temperatures suitable to the required ware, the temperature being observed by the use of Seger cones. Such experiments generally commence at 950°, and may proceed to any desired temperature. Observation is especially directed to the changes which the clay undergoes, particularly as to appearance, colour, porosity, contraction, and fusibility. As regards the appearance of the fired clay, it should be free from cracks or blisters, and should be homogeneous in colour. Cracks may be due to excessive plasticity, to its reverse, excessive shortness, or to the presence of too coarse particles. The first of these defects is indicated by excessive contraction; it may come into play when the total contraction during drying and firing exceeds 12 per cent., and in such cases the clay needs to be shortened. Too short or unplastic clays also tend to crack on firing, so that the application of such clays to manufacturing purposes is limited, unless they can be used with very plastic clays (W. Burton). Where the cracks are due to coarse particles, these become evident on breaking the fired block at the crack. To avoid this fault the coarse particles must either be removed from the clay, or the whole must be finely ground.

**Evenness of Colour** is important, especially in the manufacture of fine wares. In these cases especial attention must be paid to the soluble salts contained in the clay. Sulphates, of which gypsum and sulphate of magnesium are most commonly met with, are the chief cause of colour faults in clay wares. If present, their action must be estimated by extracting the clay with slightly acidified water as follows: 100 c.c. of water and a few drops of hydrochloric acid are added to 25 g. of the clay-powder in a porcelain dish; if carbonates are present in the clay, they must first be decomposed by covering the dish with a clock-glass and warming. The extraction of the soluble sulphates is carried out by warming the dish and its contents on the water-bath, and repeating the treatment with acidified water until a filtered sample ceases to show the presence of sulphuric acid. When the clay has been completely extracted, the total washings are warmed and filtered.<sup>1</sup> The filtered liquid is brought to a definite volume either by dilution or evaporation, and half of the solution used for the determination of the sulphuric acid, and the other half for the determination of the calcium and magnesium. If, however, carbonates are present in quantity, the following method of determining the soluble

<sup>1</sup> An excellent filtering apparatus for this purpose is described by J. W. Mellor, *Trans. Eng. Ceramic Soc.*, 1906-7, 6, 54.

salts should be used: the clay is extracted with pure water, the turbid wash-water decanted and lime water added to the decanted liquid, and the whole saturated with carbon dioxide. The liquid is then boiled, when the reprecipitated calcium carbonate carries down the fine clay and clarifies the liquid. The clear filtrate from the precipitate can then be used, as described above, for the estimation of sulphuric acid, calcium, and magnesium, or for the determination of all the soluble salts present.

When the amount of sulphates in a clay may give rise to defects of colour, the clay must be treated, in actual use, with a corresponding amount of a barium salt, to produce a uniform colour. For this purpose, barium carbonate or barium chloride are generally used; the former is usually preferred, as no bad effects follow from the employment of a slight excess of this compound. In the case of barium chloride it is necessary to add exactly the amount required to correspond to the sulphuric acid present, but it is usual to employ as much as twice the theoretical amount of barium carbonate; the addition is made before the clay is fashioned into shape. In some works it is customary to use the carbonate and chloride of barium together, thus avoiding any excess of the chloride.

Colour defects due to sulphates may also arise from the simultaneous presence of calcium carbonate and iron pyrites in a clay. In presence of air and moisture, sulphates are formed by interaction from these two substances, so that, where such clays are to be used, they must not be exposed to the air. Finally, the presence of calcium carbonate alone has been found to cause colour defects in certain clays, giving rise to sulphate of calcium by retaining the sulphurous fumes of the fuel used in burning. Wares exhibiting these defects are generally known as "flashed" or "struck"; such colorations may usually be avoided by firing alternately with a "reducing" and an "oxidising" kiln-atmosphere, the calcium sulphate being thereby reduced.

Vanadium compounds which are found in certain clays may also give rise to defective colour in fired wares (*cf.* p. 601). The most characteristic defect of this kind is a greenish-yellow colour most frequently found in under-fired pieces. The colour generally makes its appearance as a "bloom" when the pieces are wetted, and as it is readily soluble in hot water, its nature can be easily ascertained by chemical tests. The defect can be avoided by a sufficiently intense firing.

**Colour.**—Every clay fires to a characteristic colour, but the tint depends primarily on the amount of ferric oxide contained, and further, on the ratio of the ferric oxide to the other constituents, particularly to the lime and alumina. Thus, clays rich in lime and poor in ferric oxide burn white, if the firing temperature is sufficiently high (W. Burton). Clays in which the ratio of ferric oxide to alumina is 1 : 15

also burn white; where this ratio is 1 : 10 the clays burn yellow, and if the ratio is so low as 1 : 2 or 1 : 3, lime also being low, the clay burns red. Calcareous clays burn red so long as the quantity of lime is not more than one and a half times that of the ferric oxide: clays richer in lime burn yellow, provided the firing temperature does not exceed 900°. In these statements it is assumed that all the constituents of the clay are in a state of fine division.

**Density.**—A measure of the closeness which a clay assumes on firing may be obtained by a determination of its porosity. Generally, though by no means invariably, the higher the firing temperature the denser will be the fired clay. To obtain an idea of the behaviour of a clay in this respect, the porosity (*cf.* p. 591) of sample blocks is determined, after firing at different temperatures. For this purpose each block is weighed, the weight and firing temperature noted on the block in pencil, and the blocks then placed in boiling water. In order that the pores of the clay blocks may be completely filled, the samples are left in the water, with the top edge just uncovered, for at least twelve hours. When cold they are taken out, the superficial moisture removed with a cloth, and again weighed. The difference in weight is, of course, that of the absorbed water; it may be expressed as a ratio of the original weight of the blocks, so as to give a measure of the comparative porosity.

**Vitrification**, which means the attainment of the greatest and most complete closeness of the particles of a fired clay, is of great importance in judging the working properties. When a clay has attained complete density or closeness, it should absorb only the most minute amount of water. This closeness of texture produced by vitrification, is roughly classified by reference to the properties which various clays or mixtures assume when they are sufficiently fired, and the term is accordingly applied to the closeness of the texture of porcelain, earthenware, or bricks respectively. The fracture of a perfectly fired example serves as a good guide, and the conchoidal fracture of porcelain, the earthy fracture of earthenware, or the lustrous or hackly fracture of paving bricks are regarded as characteristic of different degrees or of different types of vitrification. The vitrification point of a clay, *i.e.*, the temperature at which it begins to fuse, must not be confounded with its melting point. Generally speaking, the greater the temperature interval between vitrification and melting of any particular clay, the more suitable it is for manufacturing purposes. Some clays tend towards intumescence on firing, so that at a certain point they swell considerably and lose their shape; when broken, after firing, such clays are coarsely porous, like pumice-stone. This intumescence is due to a sudden development of gases at the softening point of the clay, which are unable to escape as rapidly as they are formed. This fault may generally be



remedied by adding suitable aplastic materials to the clay, and by slow firing.

**Firing Contraction** is the term applied to the contraction clay undergoes when fired. This property varies with the temperature reached, and is determined, as in the case of "drying contraction," by contraction marks. The amount of contraction depends chiefly on two factors which work in opposite directions, viz., the contraction of the clay-substance and the expansion of the quartz; the contraction will be greater or less, according as one or other of these factors preponderates. This statement only applies to clays poor in alkalis or lime; in clays or clay mixtures containing such constituents, the formation of fusible silicates also plays an important part if the firing is carried to a sufficiently high temperature (W. Burton). A clay rich in quartz particles and poor in clay-substance may even expand on firing. The contraction or expansion, as the case may be, is generally expressed as a percentage of the length of the fired block, as in the case of disintegration.

**Refractoriness.**—This property affords information as to the temperature to which a clay may be exposed without melting and losing its form. Since all clays are refractory to a certain extent, it is usual to distinguish ordinary clays from those which are highly refractory; the latter are usually spoken of as "refractory clays." In order to arrive at an idea of the refractoriness of a clay, the only available method is to make comparative tests with clays or other substances, the behaviour of which is known. This is especially important in technical work, because the refractoriness of a clay is determined by many factors, apart from its exact chemical composition. The subject has attracted much attention among German ceramic chemists, and the work of Bischof, Richter, Seger, and others has resulted in the establishment of definite methods by which reasonably concordant results may be obtained.

Before describing either of the methods which may be used for obtaining a correct idea of the refractoriness of a clay, some general considerations are desirable which are applicable in all cases, and which must be attended to if reliable results are to be obtained. As the methods are based on a comparison with standard clays or mixtures, it is necessary to make as many points of comparison as possible. Further, the conclusions will be all the more reliable, if they are deduced from data obtained at different temperatures. Thus, besides observations made at a very high temperature, it is necessary to compare the results obtained at some lower temperature, fixed according to the results of the first determination, and subsequently a series of determinations must be made at several still lower temperatures, in order to arrive at sound conclusions as to the firing-colour, contraction, etc., that will be obtained in manufacture. Certain definite rules

the result of the cumulative work of many experimenters, which may be summarised as follows:—

1. A single ignition experiment affords insufficient ground for the formation of an opinion.<sup>1</sup> A certain and final opinion can only be arrived at by means of a series of separate determinations which agree among themselves. If the temperatures are too high or too low the results may be vitiated accordingly. Clays may apparently behave alike up to a certain point, and then one of them may rapidly break down; a result obtained at too low a temperature would, in such a case, be misleading as to the industrial application of the clay in question. On the other hand, firing a clay at too high a temperature may lead to results that would not occur in practice because of errors arising from such causes as the following:—The natural falling to dust, volatilisation of certain ingredients, the influence of the material of the crucible or of the substance used for supporting the experimental pieces or the carrying over of slag or ash, all of which are more liable to come into play at excessively high temperatures.

2. Whatever temperatures are employed for these determinations, they should be recorded with the utmost accuracy by suitable pyrometers or pyroscopes, the reliability of which has been checked.

3. As the final result can only be obtained by many separate observations, intermediate values being arrived at by interpolation, it is very necessary that more than one determination should be made at each selected temperature, and that the individual results should agree among themselves.

**Methods of Determination.**—For purposes of standard comparison it is necessary to arrange a series of substances the pyrometric behaviour of which is constant and definite; various series have been proposed for this purpose by Bischof, by Seger, and by Kreiling.

Bischof's method<sup>2</sup> is based on the use of control samples prepared from a mixture of 1 part of pure alumina with 1,  $1\frac{2}{10}$ ,  $1\frac{4}{10}$ , etc., parts of pure silica, 1 part of the best fireclay being added to the mixture in each case. The mixtures are moulded into small cylinders which are used as pyroscopes for ignition with the clay to be tested, their behaviour furnishing a scale by means of which identical experiments may be carried out with certainty and reliable results obtained.

Seger<sup>3</sup> has adapted his well-known pyrometric cones as standards of comparison, instead of the normal mixtures of Bischof. The composition of these cones, are well known to all workers in the clay

<sup>1</sup> Cf. C. Bischof, *Die feuerfesten Tone*, 1895, p. 184; also P. Kreiling's monograph, "Die Giroder Tone" (*Sprechsaal*, 1898, Nos. 7-10).

<sup>2</sup> A full description of the method is given in *Die feuerfesten Tone*, p. 142 *et seq.*

<sup>3</sup> Cf. *Collected writings of H. A. Seger*, edited by Hecht and Cramer; English translation edited by A. V. Bleininger.

industries; they possess the great advantage over normal clays that they are standardised by the German works before they are issued, and as they have become recognised articles of commerce all over the world, they afford the certainty of always having a substance of constant composition for comparison.

P. Kreiling has extended the methods due to Bischof; he considers that natural clays afford better criteria for purposes of comparison than artificially prepared mixtures such as those used by Seger. The process really involves the deduction of an unknown quantity from known data, and whilst the accuracy of the conclusions may depend on the accuracy of observation of individual ignitions, certainty in the use of such a method can only be obtained by extensive preliminary practice with well-established standards.<sup>1</sup> Kreiling contends that a carefully selected series of normal clays taken in systematic order, affords the most useful method for estimating the value of any natural clay, to the clay worker; as each normal clay should be a typical representative of a particular group of clays, it should furnish a many-sided and comprehensive standard. By the use of such standards a definite position can be allotted to an unknown clay with the greatest accuracy, and by repeated experiment it becomes possible to place the clay so accurately, by comparison with well-known standard clays, that a great deal may be learned directly about its general working properties. Further, natural clays have many advantages over artificial mixtures, especially as their fusion-phenomena are directly comparable with each other, while those of artificial mixtures are not, and the less the behaviour of a melting mass resembles that of a melting clay, the less reliable is such a mixture as a criterion of the behaviour of a clay. Against this great advantage of the use of normal clays the objection has been made in Germany that their sources are limited, and that they are not generally obtainable. The actual conditions are the very reverse of this; the normal clays that are generally used occur in extensive deposits, and are important articles of commerce.

Whatever method of pyrometric investigation be adopted, the following principles must be borne in mind if accurate results are to be arrived at.

1. Preliminary ignitions must first be made to serve as a guide for further work by indicating how the experimental steps may be most advantageously arranged; what temperatures will produce a definite change of shape; what shape and treatment of the samples may be best to adopt for the ignition, and finally, what materials are to be used as standards of comparison, or what selection of normal clays will be most useful? It then becomes a question of carrying out a

<sup>1</sup> A full discussion of all the points involved is given in P. Kreiling's monograph, "Die Giroder Tone," *loc. cit.*

series of ignitions, which must be repeated until concordant results are obtained from several experiments.

If the pyrometric tests are then supplemented by reliable analyses, the conclusions gain very much both in completeness and in certainty.

Certain characteristics of fusion are to be looked for in pyrometric observations, which form the real starting point for all the deductions. After a sample has been ignited it has to be decided, apart from changes in colour, volume, or hardness, whether any change in shape or deformation has taken place. The first sign of incipient fusion is the formation of a vitrified coating, which ranges from the slightest glassy or oily appearance of the surface to a thicker vitrified coat, extending until the mass flows, becomes enamel-like, or, finally, even glassy. In other cases signs of fusion may be found in the interior of the sample when it is broken. Thus the mass may contain isolated cavities, or it may be finely or coarsely porous or approach the condition of pumice, or it may be blistered and cavernous, according to the temperature used and the nature of the clay. When the temperature has been sufficiently high to alter the shape of the sample, it is found that with increasing temperatures the cylindrical test piece may become successively conical, spherical, hemispherical, and then drop-shaped; finally, the drop broadens out to a pad-shape, flattens, and then liquefies completely. It may be stated, generally, that if a clay melts to an enamel or glass, this may be regarded as a sign of easy fusibility.<sup>1</sup>

A furnace of the type of that designed by Deville is the most useful for these determinations.<sup>2</sup>

The clays to be tested are worked up with water, shaped into tetrahedra, and dried, or even slightly ignited. These tetrahedra are then placed alternately, either with Seger cones or with similar tetrahedra of normal clays, in a refractory crucible, the test pieces being fixed on to a refractory stand with a little mucilage, or, better still, with a thin paste of kaolin. The relative positions of the tetrahedra of clay and of the firing standards must be accurately noted. In testing clay, it is customary to begin with the lowest refractory standards, say, for instance, Seger cone No. 26, and with this, as a further control, cones No. 27 and No. 28 are generally used, with two or three cones of the clay to be tested placed between them. When these have been fixed in the crucible it is closed by the lid and placed in the Deville furnace.

The furnace is lighted with paper; charcoal is then added in small pieces, and is brought to a glow by slowly working the bellows. When

<sup>1</sup> For the special pyrometric methods of testing other refractory materials such as quartz, sandstone, graphite, etc., cf. Bischof, *Die feuerfesten Tone*, pp. 140, 141.

<sup>2</sup> Full particulars of such furnaces and their use will be found in C. Bischof's *Die feuerfesten Tone*, p. 131 *et seq.*, and in Seger's *Collected writings*, vol. i., p. 222 *et seq.* Cf. also H. O. Hofmann, *J. Soc. Chem. Ind.*, 1895, 14, 969.

glowing has started, small coke or gas-retort carbon is added in weighed quantities, and the treading of the bellows carefully regulated by the watch, so that a definite number of treads are made per minute. A still better plan is to regulate the air-blast by means of a manometer attached to the apparatus.

The ignition is continued until the crucible becomes distinctly visible again. It must then be withdrawn from the red-hot furnace and opened; if the lid is fused on to the crucible, it must be carefully removed with a chisel, every precaution being taken not to scatter or disarrange the contents. The appearance of the test pieces indicates whether the temperature has been sufficient to afford definite information. In general, 900 g. of gas-retort carbon or 1 kg. of coke are sufficient to fuse Seger cone No. 26. If further ignitions are necessary, 100 g. more coke or retort carbon are taken each time until the clay to be tested melts. After each experiment the ash, etc., left in the furnace is removed, so that the furnace is immediately ready for the further ignitions. While good coke may be employed as fuel, the use of gas-retort carbon is recommended, as it leaves only minute quantities of ash, and it is a highly concentrated fuel which allows high temperatures to be reached more easily than with coke.

The "Kryptol" furnace and the Ohio Electric furnace may be employed in place of the Deville furnace (W. Burton).

## CHEMICAL ANALYSIS

### I. TOTAL OR CENTESIMAL ANALYSIS

Total analysis affords information on the composition of a clay with regard to the proportions of the various basic or acidic oxides present. This is generally attained either by fusion with alkali carbonates, or by treatment with hydrofluoric acid or with ammonium fluoride. The results of both methods need supplementing by a determination of the loss on ignition, and if necessary, of the contained sulphuric acid, sulphur, carbon dioxide, etc.

#### 1. Fusion with Alkali Carbonates.

For this purpose a mixture of potassium and sodium carbonate in molecular proportions is generally used; other proportions have often been suggested, and the use of sodium carbonate alone has also been advocated, but the mixture in molecular proportions is the most useful. From 1 to 2 g. of the finely powdered clay, dried at 120°, are weighed into a platinum crucible, 1 g. of the mixed carbonates added and stirred into the clay powder carefully with a glass rod. This operation is

repeated until from six to ten times the weight of the clay taken has been added and the mixture looks perfectly homogeneous. The glass rod is then cleaned by rolling it round in a further small quantity of the fusion mixture, which is added to the mixture in the crucible. The covered crucible is then warmed over a small Bunsen flame and the temperature gradually increased up to a full red heat, whereby the mass is gradually fused. When the contents of the crucible are in a state of tranquil fusion, the heat is withdrawn and the crucible allowed to cool; strong ignition over the blowpipe is unnecessary, and should therefore be avoided. When the crucible is cold, the bottom should just be raised to a dull-red heat, twice successively, by applying a small Bunsen flame; this proceeding facilitates the removal of the melt from the crucible. When the crucible and its contents are again cold, a few c.c. of distilled water are poured in and heat again cautiously applied, the melt being watched all the time, so as to avoid any bumping or spitting; after a few minutes the melt will become detached from the crucible. The contents of the crucible are then washed into a large platinum dish, covered with water, the dish covered with a clock-glass and heated on a water-bath until the melt is completely softened. Hydrochloric acid is then added in small quantities at a time, so as to avoid excessive effervescence, and when excess of the acid has been added, the solution is filtered off and the filtrate evaporated to complete dryness on a water-bath. In the later stages the drying is facilitated by constant stirring with a glass rod, so as to keep the residue in a fine powdery state. When all the hydrochloric acid has been driven off the powdery residue is heated for an hour in an air-bath at  $120^{\circ}$ . It is generally necessary to treat the residue a second time with hydrochloric acid and evaporate down to dryness again, so as to ensure the separation of the silica (W. Burton). When cold, the contents of the dish are again moistened with moderately strong hydrochloric acid and allowed to stand for one hour; water is then added and the contents of the dish warmed on the water-bath until the supernatant liquid is clear. The solution is then poured through a filter and this treatment repeated until the residue remains colourless on being moistened with hydrochloric acid. The residue, which consists of *Silicic acid*, is transferred to the filter and washed with hot water until the filtrate no longer reacts with silver nitrate solution. The filter and contents are placed in a platinum crucible while still moist, and first carefully dried over a small flame; the filter is then incinerated by stronger heating, and the crucible finally strongly ignited till its weight is constant; it is advantageous to use a Teclu burner for this purpose.

If the clay contains *Titanic acid*, it will accompany the silica, and may be separated from the latter by means of hydrofluoric acid or of ammonium fluoride. To effect this separation the contents of the

crucible are covered with strong hydrofluoric acid, a few drops of sulphuric acid added, the crucible warmed on the water-bath until the silicon fluoride has volatilised, the sulphuric acid evaporated off, and the residue weighed; the titanitic oxide should be identified qualitatively by the violet coloured bead formed with microcosmic salt. If alumina has remained with the silica, the contents of the crucible are not evaporated quite to dryness, but the evaporation is interrupted when sulphuric acid fumes begin to volatilise; the contents of the crucible are then diluted considerably with water, and warmed on the water-bath; by this treatment titanitic acid separates out, while the alumina goes into solution and can be precipitated by ammonia.

It is convenient to divide the filtrate from the silica into two parts; one half is used for the determination of iron, the other for the determination of alumina; a 400 c.c. flask is useful for this purpose, the contents of which can be conveniently divided by means of a 200 c.c. pipette; each portion is transferred to a platinum or porcelain dish for analysis.

To precipitate *Alumina and Oxide of Iron* the dish and contents are warmed on the water-bath, a distinct excess of ammonia added, drop by drop, to the hot solution, and the warming continued until the odour of ammonia has disappeared;<sup>1</sup> the clear supernatant liquid is filtered off, the precipitate collected on the filter paper and washed several times with hot water. To prevent a separation of alkaline earths at this stage, complete washing is not insisted upon, but the precipitate is washed back into the dish, dissolved in hydrochloric acid, and the precipitation repeated; the precipitate is then washed with hot water until no reaction is obtained with silver nitrate. The following points should be observed in the estimation:—precipitation in the hot solution; addition of ammonia in distinct although slight excess, whereby the time occupied in driving off the ammonia on the water-bath is reduced to a minimum, and the precipitate thus prevented from becoming gelatinous; hot water must be used for washing, and the washing repeated immediately the water previously added has disappeared from the contents of the filter; washing must be carried out in such a way that the jet of hot water always promotes the breaking up and suspension of the precipitate. When the precipitate is thoroughly dry, it is detached from the filter paper by scraping, and collected in a platinum crucible; the filter paper is incinerated separately and the ash added to the contents of the crucible. The whole is then strongly ignited till the weight is constant; the quantity found is doubled for the calculation of the amount of ferric oxide and of alumina present.

*Ferric oxide* is determined either by reduction with zinc and titration with potassium permanganate solution, or by iodimetry. If the former

<sup>1</sup> This treatment differs from the improved method given by Lunge. (Cf. p. 610.)

method is used, the second half of the filtrate from the silica is treated with an excess of sulphuric acid, evaporated on the water-bath till the hydrochloric acid is driven off and the residual solution washed into a small flask, reduced with zinc and titrated with permanganate solution, 1 c.c. of which corresponds to 1 mg. ferric oxide (*cf.* pp. 99 and 380). If the iodimetric method is employed, the contents of the dish are concentrated on the water-bath without addition of sulphuric acid, and then estimated as usual.

If *Manganese* is present in appreciable amount (most clays contain traces), the second precipitation of alumina and ferric oxide is carried out with sodium acetate. Ammonia is first added to the solution until a precipitate begins to form; an excess of sodium acetate is then added, and the solution heated on the water-bath until the basic acetates separate; the precipitate is then filtered off and washed, as in the case of the ammonia precipitate. The manganese is precipitated from the filtrate by bromine water and ammonia, the precipitate filtered, washed, ignited, and weighed, and calculated as  $Mn_3O_4$ .

For the determination of *Calcium*, ammonium oxalate solution is added to the concentrated filtrate from the manganese whilst still hot, the precipitate filtered off, thoroughly washed with hot water, strongly ignited, and weighed as  $CaO$ . It is advantageous to use a Teclu burner for the ignition, as it permits of the rapid and complete transformation of a fairly large quantity of calcium carbonate into the oxide, provided a small platinum crucible is used.

*Magnesium* is precipitated from the concentrated filtrate by sodium phosphate and ammonia in the usual way (*cf.* p. 406). The precipitate is filtered off, dried, removed from the filter paper as completely as possible, and collected in a porcelain crucible; the filter paper is burnt in a platinum wire, and the ash added to the crucible. The crucible is then covered with a platinum lid, and ignited till its weight is constant. The ignited precipitate consists of  $Mg_2P_2O_7$ ; 100 parts  $Mg_2P_2O_7 = 0.3624$  parts  $MgO$ .

## 2. Treatment with Hydrofluoric Acid.

The treatment with hydrofluoric acid or with ammonium fluoride serves to determine the alkalis in a clay. About 5 g. of clay, contained in a platinum dish, are moistened with water, and digested on the water-bath with concentrated hydrofluoric acid and sulphuric acid, until the former is evaporated, and the sulphuric acid remains behind. The dish is then carefully heated over a free flame until the sulphuric acid fumes strongly. The sulphates thus formed are dissolved in water, and any coarse granules of quartz which may be present, and which generally take a fairly long time to dissolve in hydrofluoric acid, filtered off. A few drops of nitric acid are added to the filtrate to



oxidise ferrous iron, and if the separate determination of each is not required, the alumina, ferric oxide, and calcium are precipitated together by ammonia and ammonium carbonate. The solution and precipitate are then washed into a litre flask, diluted to the mark, and mixed by shaking. When the precipitate has settled, 500 c.c. of the clear liquid are drawn off by a pipette, transferred to a platinum dish, evaporated to dryness on the water-bath, and the ammonium salts completely driven off by stronger heating. The residual salts are dissolved in water, the magnesium precipitated either by Schafgotsch's solution (a solution of 235 g. of ammonium carbonate and 180 c.c. of ammonium hydroxide of sp. gr. 0.92 in 1000 c.c. of water) or, according to Classen,<sup>1</sup> by ammonium oxalate in acetic acid solution, the solution filtered, the filtrate again evaporated, and the residue ignited. The alkalis are thus obtained as sulphates, and are weighed as such. The total alkali present is obtained by difference, after determining the contained sulphuric acid. In most cases this estimation of total alkali fully suffices. If the alkalis are to be estimated separately, the potassium is precipitated by platinum chloride after the determination of the sulphuric acid; it is then estimated as directed on p. 535.

If ammonium fluoride be used for the estimation of the alkalis, the weighed quantity of clay is moistened, and mixed in a platinum dish or crucible with eight times its weight of ammonium fluoride, by means of a thick platinum wire. Water is then added drop by drop in sufficient quantity to form a thick paste, which is heated on the water-bath till dry; the fluorides formed are then decomposed by sulphuric acid, the latter evaporated off, and the residue further treated as directed above.

### 3. Estimation of Other Constituents.

*Sulphuric acid.* For this estimation it is advantageous to weigh out special samples. The determination is carried out as directed on p. 573.

*Pyrites.* If the clay contains sulphur as sulphide of iron, it must be oxidised by aqua regia to sulphuric acid. About 10 g. of the clay are repeatedly evaporated with aqua regia in a porcelain dish, and the sulphates formed extracted with dilute hydrochloric acid. The solution thus obtained is concentrated, the ferric oxide precipitated by ammonia, according to Lunge's method (p. 272), and the sulphuric acid in the filtrate estimated with barium chloride. If the clay contains both metallic sulphide and sulphuric acid, the percentage of each can be calculated from the two estimations.

*Carbon dioxide* may be estimated either gravimetrically or volumetrically (cf. p. 148).

*Loss on Ignition.* About 1 g. of clay is carefully warmed, and then

<sup>1</sup> Z. anal. Chem., 1879, 18, 373; *Ausgewählte Methoden der analytischen Chemie*, vol. ii., p. 834.

ignited to constant weight, either on a Teclu burner or over the blow-pipe. The loss of weight is due, according to circumstances, to water alone, or to water plus carbon dioxide, organic matter, and to a certain extent to sulphur.

## II. RATIONAL ANALYSIS

The method of investigation of clays which has become known by the name of "rational analysis," was introduced by Forchhammer,<sup>1</sup> who examined a series of clays, by treating the ignited product with dilute sulphuric acid, and separating the soluble from the quartz-like silica by carbonate of sodium solution. Subsequently Brongniart and Malaguti adopted this method, but substituted alkali hydroxide for sodium carbonate for the separation of the two forms of silica. From 1870 onwards, Aron and Seger brought about the general adoption of rational analysis for the technical examination of clays, in Germany. These investigators also used alkali hydroxide for separating the two forms of silica, and their example was followed by many other chemists. In opposition to Michaelis' assertion that a 10 per cent. sodium hydroxide solution does not attack quartz, Lunge and Schochor-Tscherny<sup>2</sup> proved the solubility of quartz in alkali hydroxides. Subsequently Lunge, in conjunction with Millberg,<sup>3</sup> thoroughly studied the action of sodium hydroxide and of carbonate of sodium solution on quartz and soluble silica. The result of this investigation was to show that quartz (powdered rock-crystal was used in the experiments) was appreciably soluble in boiling sodium hydroxide solution. The solubility of quartz depends on its fineness of division, on the concentration of the sodium hydroxide solution, and on the duration of the heating. Quartz-dust dissolves completely in a 15 per cent. sodium hydroxide solution after thirty hours' heating. Under similar conditions, the solvent action of sodium hydroxide is stronger than that of potassium hydroxide. Even hot solutions of alkali carbonates dissolve quartz-dust, although, of course, to a less degree than the hydroxides. The silicic acid separated by treatment of silicates with acid is completely dissolved by a 5 per cent. sodium carbonate solution on heating on the water-bath for a quarter of an hour. The above investigators therefore reject the use of alkali hydroxide solutions for separating the two forms of silica; they regard the method as vitiated by great errors, and recommend the use of a 5 per cent. carbonate of sodium solution. A whole series of researches has followed these investigations, and in the main confirmed them. Thus Sabeck<sup>4</sup> admits the solubility of the finest quartz and quartz-dust in a 5 per cent. sodium hydroxide solution, but emphasises the fact that the error arising from the use of a 2 per cent. solution is

<sup>1</sup> *Pogg. Annalen*, 1835, 35, 331.

<sup>3</sup> *Ibid.*, 1897, 10, 393.

<sup>2</sup> *Z. angew. Chem.*, 1894, 7, 485.

<sup>4</sup> *Chem. Ind.*, 1902, 25, 90.

inappreciable for the purpose of technical analysis, the duration of heating being from two to five minutes; he states, however, that to attain scientifically accurate results, sodium carbonate solution must be used instead of sodium hydroxide for separating the two forms of silica. Zschokke's experiments<sup>1</sup> confirm those of Lunge and Millberg. Experiments by Berdel<sup>2</sup> on the same subject established an appreciable loss of quartz on digesting, up to boiling-point, with 15 per cent., 10 per cent., and 5 per cent. sodium hydroxide solutions; the loss on treating powdered felspar with sodium hydroxide was smaller. Berdel proposes the use of a 6 to 7 per cent. sodium hydroxide solution for separating the two forms of silica, and that the solution be heated nearly to boiling point, stirred, the supernatant liquid allowed to settle during from four to five hours, and then filtered without dilution. Koerner,<sup>3</sup> while recognising the correctness of Lunge and Millberg's investigations, states that in his experiments he could not succeed "in attaining an even approximately complete separation of quartz from combined silica by a quarter of an hour's heating on the water-bath with a 5 per cent. carbonate of sodium solution." By heating for half an hour, he obtained results which agreed fairly well with the calculated values.

With regard to the varying statements on the separation of combined silica from quartz, Kreiling is of opinion that sufficient attention has not been paid to the relative quantities of solvent and substance used. It is obvious that this factor will influence the process in a way which should not be under-estimated. On the other hand, it is well established by the above experiments, that alkali hydroxides accelerate the solution of the silica, and promote rapid settling of the residue. Kreiling therefore suggests the use of a solution of sodium carbonate containing a small quantity of sodium hydroxide as suitable, the heating on the water-bath being limited as much as possible. In this way the two forms of silica formed from clay by the action of acid are separated with ease and certainty, without any fear of appreciable quantities of quartz going into solution. For this method a solution containing 10 per cent. of crystallised soda (corresponding to 3.6 per cent. sodium carbonate), and 1 per cent. of sodium hydroxide suffices.

The work of Lunge and Millberg also gave rise to experiments on the use of sulphuric acid to decompose clay-substance. The varying statements of Seger as to the concentration of the sulphuric acid to be used, caused Sabeck to investigate the correct conditions. Seger<sup>4</sup> states that for 5 g. of clay he takes 100 to 150 c.c. of water and 50 c.c. of concentrated sulphuric acid, but in another communication<sup>5</sup> he gives

<sup>1</sup> *Baumaterialienkunde*, 1902, Nos. 10 and 11.

<sup>2</sup> *Sprechsaal*, 1903, 1371.

<sup>3</sup> *Beiträge zur Kenntniss der Elsasser Tone*, Inaug. Dissert. Strassburg, 1900.

<sup>4</sup> Cf. *Collected writings*, loc. cit.

<sup>5</sup> *Sprechsaal*, 1903, 1371.

from 100 to 200 c.c. of water to 50 g. of sulphuric acid and 5 g. of clay as the relative quantities to be taken; accordingly he does not appear to have considered the concentration of the acid as a material factor. According to Sabeck's experiments the proportion of 100 parts of water to 50 of sulphuric acid is the best; violent bumping on heating is thereby largely prevented, and any considerable sinking of the level of the liquid is avoided; where the level of the liquid sinks, the particles of clay left sticking to the sides of the dish escape the action of the acid. Sabeck states, and has proved by experiment, that Seger's view that clay-substance is not attacked by concentrated sulphuric acid, is erroneous. On treating argillaceous material with 100 c.c. of water and 50 c.c. of sulphuric acid, and boiling for four hours, the felspar remains practically unattacked, another fact in favour of this concentration. Berdel has proposed the same concentration of acid. If the clay contains organic matter, the addition of nitric acid is serviceable. Various proposals have been made to soften the clay in water with addition of sodium hydroxide solution, in order to facilitate the breaking up of the clay; Kreiling does not consider such a treatment necessary, as decomposition fully succeeds without it.

As regards the procedure of rational analysis, the following method is advantageous and easily carried out. About 5 g. of clay, dried at  $120^{\circ}$ , are covered with 50 c.c. of water in a platinum or porcelain dish of about 250 c.c. capacity, and the clay thoroughly disseminated by stirring with a glass rod or thick platinum wire. Fifty c.c. of concentrated sulphuric acid are then added and mixed in; the liquid becomes warm, whereby the division of the clay is promoted. Finally, the remaining 50 c.c. of acid are added, and the whole again mixed. The dish is then covered with a clock-glass, heated over the free flame until its contents boil, and the heating continued until the sulphuric acid fumes strongly. The contents of the dish are then allowed to cool, diluted with water and stirred; after a short time the supernatant liquid becomes clear enough to be filtered off. The residue is moistened with hydrochloric acid, water added, and after stirring, the dish placed on the water-bath, and warmed for about fifteen minutes; the supernatant liquid is then filtered off, and any solid matter which may have passed on to the filter, washed back into the dish. This treatment is continued so long as the residue colours the hydrochloric acid poured on to it. The residue is then transferred to the filter, thoroughly washed with hot water, then washed back into the dish, and the contained liquid diluted to 250 c.c. Crystallised sodium carbonate is then added in the proportion of 10 g. to 100 c.c. of liquid, the dish warmed on the water-bath for from one to two minutes, and then 1 g. of sodium hydroxide added for every 100 c.c. of liquid. After one to two minutes the liquid begins to clear, whereupon the dish is taken from the water-bath, and the

supernatant clear liquid decanted through a filter. This treatment with alkali solution must be repeated several times to make certain that the silica liberated by the acid treatment is completely dissolved; for example, the silica which separates from 5 g. of Zettlitz kaolin requires three such treatments to completely dissolve it. Finally, the residue still left is transferred to the filter and thoroughly washed with water containing alcohol, or with dilute ammonia. A wearisome decantation process is rendered superfluous by carrying out the rational analysis in this way, and the method is rapidly completed without appreciable quantities of quartz being dissolved.

The presence of organic matter is generally indicated by the dark colour of the clay; in such cases several c.c. of nitric acid must be added to the dilute sulphuric acid used in the decomposition.

Should the clay contain calcium carbonate, it must be removed before the decomposition. This is effected by extracting with dilute hydrochloric acid, as is directed in connection with the estimation of sulphuric acid (*cf.* p. 573).

The ignited and weighed residue represents the amount of quartz and felspar present. To estimate each of these constituents separately, the residue must be treated with hydrofluoric acid or with ammonium fluoride (*cf.* p. 583), and the alumina in the decomposed mass estimated as directed on p. 582. The amount of alumina found, multiplied by 5.41, gives the amount of felspar present; the difference between this and the total residue corresponds to the amount of quartz present, provided the residue contains no mica or similar mineral detritus.

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## CLAY WARES USED FOR BUILDING PURPOSES; EARTHENWARE AND GLAZES

By K. DÜMLER, Charlottenburg. English translation revised by W. BURTON,  
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METHODS of investigating both the physical and chemical properties of clay wares and glazes, especially in those forms which are used in connection with buildings or as actual building materials, are required for a variety of purposes. As all the most useful methods are comparative in character, it is necessary that they should be carried out under identical conditions, to afford reliable results. In Germany conferences have been held from time to time, at which the various methods have been discussed by manufacturers, architects, and engineers, with the result that certain standard methods have been agreed upon for the determination of the physical and mechanical properties of such materials, which are sufficiently accurate for practical purposes. These are recorded in the reports of the conferences held at Munich, Dresden, etc.<sup>1</sup>

No standard methods have been adopted in this country, but those agreed to by the German manufacturers are recognised as reliable and applicable to English manufactures, and are accordingly generally made use of in carrying out the specific determinations described below.

The physical investigations which may be necessary include determinations of density, structure, hardness, solidity, and resistance to fire and to weather. The chemical investigations comprise, besides general chemical analysis, the determination of the presence or absence of injurious substances, and of soluble salts, and the behaviour of the material towards acids.

### PHYSICAL EXAMINATION

The actual dimensions of the test pieces are first determined and recorded. The sample is then dried on a hot plate or sand-bath, allowed to cool, and weighed.

<sup>1</sup> The reports are published by T. Ackermann, Munich.

## I: DENSITY

## 1. Specific Volume.

The specific volume is the volume occupied by 1 g. of the material, including porous interstices. The specific volume of samples bounded by plane surfaces, such as bricks, can be determined from the dimensions and the absolute weight.

According to the decisions of the German conferences mentioned above,<sup>1</sup> the specific volume is to be determined with specimens saturated with water, by measuring the volume of water which they displace. In those exceptional cases where saturation with water may give rise to considerable loss by solution of salts, the specific volume is to be determined in the volumenometer, after coating the specimen with paraffin.

The volumenometer of W. Michaelis may be used for the determination.<sup>2</sup> The apparatus consists of a conically turned, metal box, with a turned metal lid ground to fit, which carries a graduated tube; a clamp holds the apparatus together and keeps it air-tight. The capacity of the box up to the first graduation mark on the tube is 400 c.c., and the tube itself is graduated into 100 c.c. Four delivery pipettes of 200, 100, 50, and 20 c.c. respectively, are provided. The apparatus permits of the use of fairly large specimens, ranging up to 500 g. in weight. (Cf. p. 670.)

The dried sample, after having been weighed as directed above, is placed in water for twenty-four hours or, if necessary, is coated with paraffin; in the latter case, the weight of paraffin used is determined by a subsequent weighing. The sample is then dried superficially with a cloth and placed in the metal box, the lid, the edges of which have been greased, pressed on, and the apparatus clamped tight; water is then added from the measuring pipettes, until its position can be read off on the graduated tube. The volume of the sample is given directly by the volume of water required to fill the apparatus to the first graduation mark.

## 2. Specific Gravity.

The specific gravity denotes the weight of 1 c.c. of the substance, exclusive of its porous interstices; as the weight of 1 c.c. of water is 1 g., the weights are, of course, directly comparable.

The methods decided on by the German conferences<sup>3</sup> state that the specific gravity shall be determined after reducing the substance to powder, passing it through a sieve of 900 meshes per sq. cm., and

<sup>1</sup> *Protokoll*, 20th Sept. 1890; cf. *Deutsche Töpfer und Ziegler Zeit.*, 1893, No. 34.

<sup>2</sup> Cf. *Deutsche Töpfer und Ziegler Zeit.*, 1879, No. 13.

<sup>3</sup> *Protokoll*, 20th Sept. 1890; cf. *Deutsche Töpfer und Ziegler Zeit.*, 1893, No. 34.

removing the dust by passing it through a 4900-mesh sieve. The intermediate grains are used for the determination. Two hundred and fifty g. are weighed out into the Michaelis volumenometer and 100 c.c. of distilled water added to cover the powder; the apparatus is then completely closed, struck repeatedly against a soft pad placed beneath it to remove adherent air-bubbles, and the whole allowed to stand for twenty-four hours. A further 200 c.c. of distilled water are then added from the pipette, and the position of the water read off on the calibrated tube. If, for example, the water in the tube stands at 415 c.c., since 300 c.c. of water have been added, the powder must occupy the volume of 115 c.c.

The specific gravity would therefore be  $\frac{250}{115} = 2.17$ .

### 3. Specific Porosity, or Water-absorption.

A distinction is drawn between the amount of water which any pottery body will absorb either by volume or by weight. To determine porosity the dried specimen is accurately weighed and immediately placed in water at the ordinary temperature. At first the piece should only be half immersed, but after twenty-four hours more water is gradually added until it is covered. It is then allowed to remain covered for another twenty-four hours, taken out, superficially dried with a cloth, and again weighed. The increase in weight is, of course, that of the absorbed water. The percentage proportion of this weight to the original weight of the sample is taken as representing the *absorptivity by weight*.

The *absorptivity by volume* can be determined from the specific volume of the sample, after calculating the weight of the water absorbed, to volume.

For the examination of building materials, the German conferences recommend that ten samples be taken for the determination of porosity, and that this be calculated both for weight and for volume as above.

In estimating the value of vitreous clay products, a statement of their porosity is often desirable. For this purpose the wares must be freed from glaze, if they have been glazed. The weighed sample is then placed in water, which is kept at the boiling-point for twenty-four hours to ensure its penetration; when cold, it is treated as described above; the percentage weight of the absorbed water is generally used as a measure of the porosity.

### 4. Permeability to Water.

The determination of the permeability of unglazed materials and of their surface-absorption has been generally applied to the testing of roofing-tiles in regard to their suitability for use, but these tests may



also be employed for other substances. The decisions of the German conferences<sup>1</sup> lay down the stipulation that the samples shall be of such a size as to be capable of absorbing from 20 to 25 c.c. of water, and that they shall be thoroughly dried and the edges coated with wax or paraffin for the test.

A cylindrical glass tube of 10 sq. cm. internal section is then fixed on to the upper surface of the sample by means of wax, and the following data recorded:—

1. The time required for the absorption of 10 c.c. of water, delivered into the tube from a pipette.
2. The time which elapses between the addition of another 10 or 15 c.c. of water and the appearance of dew on the under surface of the sample.
3. The time which elapses between the addition of another 10 c.c. of water in the tube and the formation of drops on the under surface, or as an alternative, the quantity of water which drops into a beaker placed below the sample.

## II. STRUCTURE AND HARDNESS

### 1. Structure of the Material.

This examination includes the observation of any flaws that may be present in the sample, as well as the nature of its fracture, from which the homogeneity of the material may be deduced. In clay wares fractures may be distinguished as conchoidal, uneven, or smooth, or as porcelain-like, earthenware-like, or earthy. In connection with the structure of the material, any flaws must be observed which may have originated in the shaping, the drying, or the firing, and the cause of such faults should be referred to their true source. In some cases the internal structure may resemble that of puff paste, or it may have a flaky, roll-like, or wavy appearance; the latter fault occurs sometimes in plastic-pressed bricks, tiles, etc. The external surface of the article may be characterised as smooth or rough; if the roughness of the surface, and particularly of the edges, is regular and considerable, it is spoken of, in Germany, as "Dragon's-toothed."

### 2. Flaws in the Glaze.

In the examination of glazed wares, "crazes" and other external flaws come under consideration. To make the finer "crazes" distinctly visible, a coloured substance is rubbed over the surface. With light-coloured glazes it is best to select a dark powder such as graphite, and for dark-coloured glazes such a material as powdered talc; these powders when rubbed into the lines or pits in the glaze render them

<sup>1</sup> *Protokoll*, 20th Sept. 1890.

more apparent. A magnifying glass should be used to assist in the examinations under both 1 and 2.

### 3. Hardness.

The hardness of clay wares is of some importance, especially in connection with building materials. It is determined according to Mohr's scale, which is generally followed by petrologists; the values in this scale are:—Talc=1; gypsum=2; calcspar=3; fluor-spar=4; apatite=5; orthoclase=6; quartz=7; topaz=8; corundum=9; diamond=10.

For the determination an attempt is made to scratch the sample with each of these minerals in turn, commencing with the hardest, which in the case of clay wares need not generally be higher in the scale than topaz. The minerals are tried in descending order until one is reached which does not scratch the sample. An attempt is then made to scratch this mineral with the fired ware. If it scratches the mineral the sample is again tried as a check on the next harder mineral of the scale, and in this way its position is fixed. The result is expressed in the figures of the Mohr's scale; *e.g.*, hardness=7. If the hardness exceeds, say, 7, but is not equal to 8, it is generally expressed as, hardness=7.5 or 7 to 8.

## III. RESISTANCE TO WEAR

This examination is generally applied to such materials as flooring tiles, clinkers, paving bricks, and blocks, etc. The wear may depend on exposure to friction, as in the case of flooring tiles, or to shock, as in the case of clinkers and paving bricks; in the former instance, friction is opposed by the hardness of the material; in the latter, shock is opposed by its toughness.

### 1. Resistance to Friction.

This is determined by grinding on an emery disc.<sup>1</sup> The disc is mounted so as to run at a definite and ascertained rate, and the specimen, which must have a grinding surface of 50 sq. cm., must be mounted under a definite pressure. For the grinding, 20 g. of Naxos emery are used for every 22 revolutions of the disc; the disc has a radius of 22 cm., is driven at the rate of 22 revolutions per minute, and should make 450 revolutions during the experiment. If these conditions are accurately observed good comparative results can be obtained. The loss of weight of the sample is expressed either in grams or in cubic centimetres.

<sup>1</sup> Cf. Böhme, "Untersuchungen über künstliche Steine," *Mittheilungen aus der Königlichen Versuchsanstalt*, 1891, p. 153.

## 2. Toughness.

This determination is widely applied in the United States, under the term "Rattler Test"; the test is not in use here. Different local authorities prescribe different rules, but the methods are identical in principle. A ball-mill, or sometimes a strong barrel of definite dimensions, is used, which is revolved mechanically at a definite speed, say 15 to 20 revolutions per minute. The paving bricks or blocks to be tested are introduced into the mill with a number of iron balls of definite shape and weight; after a specified number of revolutions the specimens are removed and the loss of weight, expressed as a percentage of their original weight, is taken as a measure of the wear.

## IV. DURABILITY

Under the heading of durability those qualities are grouped together, which are especially required in clay materials used for building purposes, such as resistance to pressure, as applied to bricks, building blocks, drain pipes, roofing tiles, etc., and resistance to the weather, permanence during frost, fire-proof qualities, etc.

Resistance to deformation under pressure is an important property of materials used in construction; the tests are best carried out by means of hydraulic or mechanical presses, many forms of which have been devised for this purpose.

Testing machines for determining tensile strength, crushing strength, and also for testing sanitary pipes, are made by a number of firms.<sup>1</sup>

The hydraulic press of Brinck and Hübner of Mannheim is made in different sizes, ranging up to one capable of exerting a maximum pressure of 150,000 kg. The plates of the press rest in hemispherical sockets, so that the pressure is always exerted in a truly perpendicular direction. The pressure is read off by means of a pointer manometer, one side of which indicates the pressure in atmospheres, and the other in kilos. When the sample breaks, the pointer remains stationary, and the pressure attained can be read off on the manometer.<sup>2</sup>

### 1. Resistance to Pressure.

This determination is carried out with cubical samples; with bricks, for instance, this form is obtained by cutting the sample in two and superposing the two portions. Thin layers of pure Portland cement are then applied to the superposed faces, and to the surfaces to which the pressure is to be applied; these bind together the two halves, and

<sup>1</sup> A suitable testing machine is made by Sir W. H. Bailey & Co., Salford.

<sup>2</sup> S. Amsler's press made by Laffon & Son, Schaffhausen, is also largely used for this purpose.

ensure the parallelism of the pressed surfaces. This test is generally applied to dry samples, but it may also be applied to samples saturated with water; in either case it is advisable to test at least six samples.

## 2. Testing Pipes for External Pressure.

There are various ways of conducting this test, and the particular method is often prescribed by the purchaser. In the Royal Mechanical and Technical Experimental School at Charlottenburg a hydraulic press is used. The pipes are capped above and below with pine boards 10 cm. wide, to which the pressure plates are directly applied. The perpendicular and horizontal dimensions of the pipes are then carefully measured under varying pressures.

## 3. Testing Pipes for Internal Pressure.

This test is also conducted in various ways. In Rudeloff's method<sup>1</sup> the pipe ends are provided with leather covers, which are made tight by a coating of gelatine; cylinders of iron and wood are connected with these leather covers, one of which is bored to receive the pressure pipe. To secure a firm grip for the leather covers the pipe is placed between two cross-bars, and these are pressed against the cylinders by a coupling rod, so that they do not come in contact with the ends of the pipe itself.

## 4. The Breaking Strength of Roofing Tiles, etc.

The method approved by the German conferences is as follows:—The lower surface of the tile is provided with two strips of Portland cement, each 1 cm. wide, and with a clear interval of 20 cm. between them, and a similar strip of Portland cement is applied in the middle of the upper side. The tile is then supported on the under strips and the load applied to the upper strip.

# V. DURABILITY TOWARDS WEATHERING

The object of this examination is to determine the influence of weathering on building materials.

## 1. Examination for Detrimental Enclosures.

The following materials are the most important detrimental enclosures:—calcium carbonate in lumps, iron pyrites, and gypsum; when burnt, these may easily cause the articles to crack on being exposed to the moisture of the atmosphere. In testing, the samples are placed under

<sup>1</sup> *Mitteilungen aus der Königlichen Versuchsanstalt*, 1892, p. 101.

a large glass shade which dips into a vessel filled with water, which, however, does not come into contact with the objects. If no cracks are observed in the course of eight days, it may be concluded with certainty that none of the above detrimental admixtures are present. Still, it is well to test a sample of the raw material whenever possible. For this purpose the raw material is disintegrated under water, and the fine portions poured through a 900 sq. cm. mesh sieve; the residue on the sieve is carefully washed, dried, and weighed, and is then tested for the above substances.

The German conferences have decided that, in addition to being identified in the raw material, the presence of such injurious constituents shall also be determined in the finished products in the following way:—The samples are treated with superheated steam of a quarter atmosphere excess pressure for three hours; for this purpose fragments of the samples are so arranged in a Papin digester, partly filled with water, that they do not touch the water, but only come into contact with the steam. A magnifying glass is used in these tests when necessary.

## 2. Permanence towards Frost.

The German conferences have decided that, of the samples which were saturated with water, five shall be tested for resistance to pressure (*cf.* p. 594), while the remaining five are to be placed in a freezing chamber capable of giving a temperature of at least  $15^{\circ}$ ; they are left in the chamber for four hours, taken out, and thawed in water at  $20^{\circ}$ . The particles thereby detached are to remain in the vessels used for thawing until the end of the experiment. This freezing and subsequent thawing are to be repeated twenty-five times, after which the crumbled portions are dried, weighed, and compared with the weight of the original sample. A magnifying glass must be used in this test to determine whether cracks or signs of splintering appear.

Pressure tests must then be carried out with dried tiles which have been subjected to the above frost experiments, and the results compared with the previous pressure tests of the same tiles.

Weathering also depends on the quantity and nature of the soluble salts contained in a building material; their estimation is described under the chemical methods of examination (p. 600).

J. W. Cobb<sup>1</sup> has proposed to test the liability to disintegration of glazed bricks by internal crystal formation. The brick is placed, glazed face downwards, in a warm saturated solution of sodium thiosulphate in such a way that an inch depth of the brick is immersed. After soaking, the brick is allowed to cool completely in the open air, so as to allow the thiosulphate to crystallise, and the soaking and cooling are repeated as often as may be necessary. A bad glazed

<sup>1</sup> *J. Soc. Chem. Ind.*, 1907, 26, 390.

brick begins to crack on the glazed surface, and to soften and flake in its substance after this treatment has been repeated a few times, whilst many successive treatments are necessary before a good brick is affected. A useful comparative test of the quality of the brick is thus obtained, which Cobb regards as giving similar indications to the freezing test.

## VI. "FIRE-RESISTING" QUALITIES

The term "fire-resisting" includes the fire proofness and refractoriness. When a body is able to withstand sudden heating without losing its stability, it is said to be fireproof. As fired clay wares are fireproof to a high degree, it is not necessary to test them for this quality.

Refractoriness, which is a far more important property of clay manufactures, is the resistance which a body is able to oppose to high temperatures; in this connection the process carried out in any particular furnace must be taken into consideration.<sup>1</sup> Both the nature and porosity of the article must also be considered.

The refractoriness of finished products of manufacture is tested by the same methods as are used for clays; either Bischof's method (p. 577), or that of Seger (p. 577) may be employed. A simplified form of Seger's method<sup>2</sup> is specially applicable, in which a modified method of lighting the fuel used in igniting the samples is adopted. About 30 g. of wood charcoal are placed in a spoon-shaped sieve, and heated to glowing in a Bunsen flame or in a fire; they are then introduced into the Deville furnace, and the weighed amount of fuel, coke, or graphite added, the bellows being worked slowly. The troublesome use of paper is thus avoided, the ash of which always attacks both the furnace lining and the crucible. The bellows are worked so that only forty treads are made per minute, which diminishes the work entailed.

The small samples used in this process are prepared by mixing the powdered ware with a little mucilage and moulding it into tetrahedra. It is advisable to place a broken fragment of the sample in the crucible along with the cones, especially if coarse-grained quartz has been used as an aplastic material, a custom which is still much in vogue. The tetrahedra are stuck on to the plate in the crucible with mucilage so as to fix them securely, and the normal clays or Seger cones which are to serve as standards for the examination, are arranged alternately with the samples.

<sup>1</sup> Cf. C. Schärtler, *Chem. Ind.*, 1907, 30, 57; *J. Soc. Chem. Ind.*, 1907, 26, 203.

<sup>2</sup> Cf. K. Dümmler, *Handbuch der Ziegelfabrikation*, 1900.

## CHEMICAL ANALYSIS

## I. GENERAL ANALYSIS

## 1. Determination of the Composition of Fired Articles.

The methods of chemical analysis used for clays (*cf.* p. 580 *et seq.*) are also employed for determining the composition of fired articles; rational analysis (*cf.* p. 585) is not applicable to wares after firing. Silica, titanous acid, alumina, ferric oxide, calcium, and magnesium are determined by fusion with alkali carbonates, and the alkalis by treatment with hydrofluoric acid or with ammonium fluoride.

In the cases of glazes the estimation of the following substances may also be required:—Boric acid; oxides of tin, lead, zinc, and barium; the colouring substances, antimony, copper, cobalt, nickel, chromium, uranium, phosphoric acid, and the noble metals, gold, silver, platinum, and iridium.

It is important to select a fair average sample for the analysis. In the case of glazed wares, attention must be paid to the difference between the body and the glaze, and the two constituents must, of course, be examined separately. The amount of glaze on the articles is comparatively small, and in the case of good wares it adheres very closely, so that its separation offers considerable difficulties. The method adopted is to strike off fragments of the glaze carefully with a hammer and chisel; these are collected, and any portions of the body which may still adhere to them are carefully removed by grinding. The fragments are then finely powdered in an agate mortar, and any particles of iron that may have splintered from the chisel used removed by means of a magnet; the sample is then ready for analysis. It is often impossible to procure a sufficient quantity of glaze by mechanical means, and in such cases other methods must be resorted to; lead glazes, for instance, can be decomposed by strong hydrochloric acid without the body of the ware being appreciably attacked.

If the powdered glaze contains lead, it will be completely decomposed by boiling with hydrochloric acid in a porcelain dish. Other glazes are not so easily attacked by this reagent, and must, therefore, be either fused with alkali carbonates, or treated with hydrofluoric acid or with ammonium fluoride.

If gold, platinum, or iridium are not present as colouring oxides in the glaze, but have been applied to it for decorative purposes, they may be easily recognised by their lustre. These metals are dissolved by aqua regia, and may thus be identified. If silver is used as a decorative adjunct, nitric acid alone must be used for solution.

The estimation of the individual constituents present is conducted

according to the ordinary methods of analysis. After the percentage composition has been determined, the molecular formula is calculated by dividing the percentage of each constituent by its molecular weight. The results thus obtained are arranged in separate groups, according to the number of oxygen atoms present in the respective oxides, as in the following example:—

2.5 $\text{SiO}_2$	0.25 $\text{Al}_2\text{O}_3$	0.7 $\text{PbO}$
0.5 $\text{SnO}_2$	0.05 $\text{Fe}_2\text{O}_3$	0.2 $\text{CaO}$
		0.1 $\text{K}_2\text{O}$

An idea of the proportions of the materials used in the preparation of the glaze can be obtained from its molecular formula, assuming an average composition of the minerals and chemicals which are most frequently used. Thus, for example, in the case of the above analysis, 0.1  $\text{K}_2\text{O}$ , combined with 0.1  $\text{Al}_2\text{O}_3$  + 0.6  $\text{SiO}_2$  give 0.1 molecular proportion of felspar (55.6 parts by weight); 0.2  $\text{CaO}$  correspond to 0.2  $\text{CaO} \cdot \text{CO}_2$ , or 20 parts of pure marble; 0.7  $\text{PbO}$  correspond to 155.68 parts of pure litharge. The remaining 0.15  $\text{Al}_2\text{O}_3$  may have been introduced in the form of clay, and would, combined with 0.30  $\text{SiO}_2$  + 0.30  $\text{H}_2\text{O}$ , give 0.15 molecular proportions of clay-substance which corresponds to 38.7 parts of pure kaolin. 0.05  $\text{Fe}_2\text{O}_3$ , presumably used as such, would correspond to 8 parts of  $\text{Fe}_2\text{O}_3$ ; 0.5  $\text{SnO}_2$  corresponds to 75 parts tin oxide (tin ashes). The remaining 1.6  $\text{SiO}_2$  is to be reckoned as 90 parts of pure quartz, flint, or similar material. If the substances thus calculated are mixed in the proportions given and fritted together, a glaze of the stated composition will be obtained. If potash preponderates over alumina, its origin must be traced to the use of a potassium salt, such as potassium carbonate, saltpetre, sylvine, or even potassium sulphate; if lime and magnesia are present in small quantities they may be considered as belonging to the felspar, and may be calculated with the alkali.

This method may serve as a guide, but it must be borne in mind that felspar is but little used as such in English glazes. Also the felspathic material is generally introduced as Cornish stone. The assumption that an identical formula will give an identical glaze is not always true in practice (W. Burton).

## 2. Examination for Lead.

Owing to the number of cases of lead poisoning which occurred annually in the pottery industry, a special Commission was appointed by the Home Office in 1898 to inquire into the best means of checking the injurious effects due to the use of lead in the manufacture of glazes. The report of the Commission<sup>1</sup> was followed by a series of negotiations between manufacturers and the Home Office in regard to the regula-

<sup>1</sup> Blue Book, 1899, C. 9207.



tions proposed by the latter, with the result that it was decided in 1903<sup>1</sup> that manufacturers should be exempted from liability, should a worker in their employ acquire lead poisoning, if no glaze is used which yields to a dilute solution of hydrochloric acid more than 5 per cent. of its dry weight of soluble lead compound, calculated as lead monoxide, provided the proper rules for cleanliness in the manufacture are also observed. The use of glazes which do not conform to this regulation is, however, permitted under special conditions, and compensation is payable to a worker who contracts plumbism.

The following method is prescribed for testing the glaze:—A weighed quantity of the dried material is continually shaken for one hour, at the ordinary temperature, with 1000 times its weight of an aqueous solution of hydrochloric acid of 0.25 per cent. strength. The liquid is allowed to stand for one hour, filtered, and the lead, in an aliquot portion of the filtrate, precipitated as lead sulphide and weighed as lead sulphate; the result is then calculated to lead oxide.

In Germany the manufacture and sale of glazed ware which yields any soluble lead compounds on boiling with concentrated acetic acid containing 5 per cent. of water for half an hour, is forbidden by the imperial law of 1879 for regulating the trade in food and utensils. This regulation is designed for the protection of the general public, not for the protection of the workers in lead glazes.

### 3. Estimation of Alumina.

In supplying refractory goods, a definite percentage of alumina is often agreed upon. The determination is carried out by the method described under the analysis of clay (p. 584).

## II. ESTIMATION OF SOLUBLE SALTS

This determination is applied almost exclusively to the examination of building materials made of fired clay.

The German conferences have determined that five samples, selected from the least fired, are to be used for the test; they must not have come into contact with water. The bricks or samples are to be cleaved in three directions; from each of the eight pieces thus obtained, the corner directed to the interior of the sample is to be broken off and powdered until the whole passes through a sieve with 900 meshes per sq. cm.; the powder is freed from fine dust by a 4900 mesh sieve, and is then used for the examination as follows:—

Two hundred and fifty c.c. of distilled water are poured on to 25 g. of the powder, and boiled for one hour, the water which evaporates being replaced. The insoluble matter is filtered off, thoroughly washed,

<sup>1</sup> *J. Soc. Chem. Ind.*, 1903, 22, 1374; W. Thomason, *ibid.*, 1904, 23, 470.

the filtrate evaporated to dryness, and the residue thus obtained gently ignited and weighed; it is calculated as a percentage of the weight of the sample.<sup>1</sup> The residue is then examined quantitatively for sulphuric acid, calcium, magnesium, potassium, and sodium, which are estimated by the ordinary analytical methods. It is best to dissolve the residue in water, with the addition of a few drops of hydrochloric acid, and dilute the solution to 200 c.c.; 100 c.c. serve for the determination of sulphuric acid and alkalis, the other portion being used for the estimation of the calcium and magnesium.

Vanadium compounds, which are often contained in clays in association with sulphates, produce a strong colouring effect, even in minute quantities, on fired building materials; they may be recognised by the greenish-yellow exudation which develops when the sample has been moistened. Their qualitative recognition is usually sufficient; it is seldom necessary to estimate them quantitatively. The greenish-yellow exudation is easily dissolved by hot water, forming a greenish-yellow solution from which a residue of vanadium compounds is obtained on evaporation. Vanadium compounds colour a borax bead a fine green in the reducing flame; the coloration disappears in the oxidising flame, especially when only small quantities of vanadium are present. On oxidation, with nitric acid vanadic acid is formed, which gives a chocolate-brown precipitate with ammonia and barium chloride, a bluish-black precipitate with gallic acid, and a flaky, apple-green precipitate with potassium ferrocyanide, insoluble in dilute acids.

Other soluble salts may find their way into highly porous building materials after building, derived partly from the mortar and partly from the surrounding ground. Chlorine compounds, carbonates, phosphates, and sulphates have been shown to be amongst the products which weather out in this way. Where masonry is in contact with decomposing nitrogenous matter nitrates may also soak into the bricks; potassium nitrate is, however, never present in freshly baked bricks, although it is often supposed to occur. General analytical methods are used for the identification and estimation of such salts.

### III. STABILITY TOWARDS ACIDS

A variety of methods are employed for testing the stability of wares towards acids. In the laboratory of the "Deutsche Töpfer und Ziegler Zeitung," the sample is powdered, and the powder which remains between the 900 and 4900 mesh sieves used for the determination. Twenty-five g. are placed in an Erlenmeyer flask and exposed to the action of 250 c.c. of a mixture of 10 per cent. hydrochloric, nitric, and sulphuric acids for twenty-four hours, with frequent shaking. The

<sup>1</sup> Cf. also, J. W. Cobb, *J. Soc. Chem. Ind.*, 1907, 26, 390.

supernatant liquid is then poured through a previously dried and weighed filter paper, the residue carefully and thoroughly washed with hot water by decantation, and then collected, washed, and dried at  $110^{\circ}$  until the weight is constant; the decrease in the weight of the sample gives the loss due to the contained metallic oxides.

H. Seger and E. Cramer<sup>1</sup> use the powder which remains between sieves with 64 and 121 meshes per sq. cm. respectively for this test; this is treated with ten times its weight of a mixture of 10 per cent. hydrochloric and nitric acids for twenty-four hours.

Kammerer uses a 1 per cent. mixture of hydrochloric, nitric, and sulphuric acids, which is allowed to act for forty-eight hours at the ordinary temperature; the change in weight and in physical properties of the samples is then examined.

#### IV. STABILITY OF GLAZES TOWARDS WEATHERING

This determination is carried out by a method analogous to that of Weber<sup>2</sup> for the examination of the frosting of glass. The glazed wares are exposed to the action of strong hydrochloric acid fumes, and are then examined; if any decomposition has taken place, it is shown by the formation of a white deposit on the surface of the glaze. A large bell-jar which fits air-tight on to a glass plate is used for the test. A shallow porcelain dish containing concentrated, commercial fuming hydrochloric acid is placed on the glass plate, across the rim of which two narrow porcelain or glass strips are placed, to serve as supports for the object to be tested; the samples are placed so that the glaze rests directly on the supports. The whole is then covered with the bell-jar, and allowed to stand at the ordinary temperature for from twenty-four to thirty hours; if a deposit has formed on the glaze after the lapse of this period, it is washed off with hot water, and tested qualitatively. Good glazes should stand this test without decomposition.

A somewhat modified form of this test is described by Cobb.<sup>3</sup> As, however, it may take weeks or months in the case of high-class glazed bricks, he recommends a similar comparative test with hydrofluoric acid for such materials.

#### THE EXAMINATION OF ROOFING SLATES

The following points must be considered in judging roofing slates:—Texture, hardness, resonance, porosity, micro-structure (the detection of

<sup>1</sup> Cf. M. Gary, "Röhrenprüfung," *Baumaterialienkunde*, III., Part 3, p. 35.

<sup>2</sup> *Verhandlungen des Vereins zur Beförderung des Gewerbestreiss in Preussen*, 1863, p. 131.

<sup>3</sup> *J. Soc. Chem. Ind.*, 1907, 26, 390.

enclosures of pyrites, marcasite, calcium and magnesium carbonates, and gypsum), effect of frost, and behaviour at high temperatures.

The chemical examination includes the determination of calcium and magnesium carbonates, gypsum, and sulphide of iron. A good slate should be as free from structure as possible, and should emit a clear note. The hardness should be at least 2 on Mohr's scale. The larger the quantity of enclosed minerals, pyrites, marcasite, and carbonates, the poorer will be the quality of the slate; the presence of gypsum is an indication that a decomposition has begun which will soon cause disintegration.

The two following tests are, according to Brunner,<sup>1</sup> also important for judging the quality of slates:—

1. *Imbibition Test.* For this test pieces 12 cm. long and 6 cm. wide are sawn out of the slate and placed in a beaker containing a layer of water 1 cm. deep; the beaker is covered over and allowed to stand for twenty-four hours, and the height to which the water has risen in the slate is then observed. This affords a measure of the quality of the slate; good slates do not become moist beyond a few mm. above the surface of the water.

2. *Weathering Test.* A piece of slate, 7 cm. × 3 cm., is hung freely in a glass cylinder at the bottom of which 100 c.c. of a saturated aqueous solution of sulphur dioxide are placed. Good slate will remain intact for from four to six weeks, and in many cases even for months. Disintegration, the equivalent to weathering, is due to the presence of sulphide of iron and carbonates of the alkali earths; marcasite is more injurious than pyrites.

### Chemical Analysis.

For the estimation of the sulphates and carbonates of the alkali earths, 5 g. of an average sample are digested with an excess of hydrochloric acid on the water-bath, until all the carbonates are completely decomposed. The liquid is then filtered, the residue thoroughly washed with hot water, and the filtrate diluted to 500 c.c.; 100 c.c. of this solution are used for the estimation of the alkali earths, and 200 c.c. for the determination of sulphuric acid, if present.

The carbon dioxide in combination with the alkali earths is determined either from the loss on ignition or gas-volumetrically (*cf.* p. 148), or by absorption.

For the estimation of the sulphur, 2.5 g. of a finely powdered, average sample are repeatedly digested with aqua regia by heating on a boiling water-bath in a large porcelain dish. The whole is then evaporated to dryness, the dry residue moistened with hydrochloric acid, water added, and the supernatant liquid filtered off after warming: this

<sup>1</sup> *Deutsche Töpfer und Ziegler Zeit.*, 1894, No. 47.

extraction is repeated three times, the residue then transferred to the filter, and thoroughly washed with hot water. The sulphuric acid is precipitated in the filtrate with barium chloride and weighed as barium sulphate; the amount found is calculated to sulphur after subtracting the sulphuric acid determined as above. Sixty-four parts of sulphur combine with 56 parts of iron to form sulphide of iron,  $\text{FeS}_2$ ; the presence of this substance, either as pyrites or as marcasite, can be detected by means of the polarising microscope.

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# ALUMINIUM SALTS AND ALUMINA

By Professor G. LUNGE

## RAW MATERIALS

THE chief raw materials employed in the manufacture of aluminium salts and of alumina are kaolin and bauxite. The former is examined by the methods described under *Clay Analysis* (cf. p. 580). The Society of French Paper-manufacturers<sup>1</sup> has agreed that 10 per cent. of moisture in kaolin is permissible; in England 5 to 6 per cent. is considered admissible, and in Germany 8 per cent.

**Bauxite.**—Schneider and Lipp<sup>2</sup> give the following directions for the analysis of bauxite:—One part of the sample is fused with five to ten parts of sodium carbonate, the melt softened in water, and evaporated with sulphuric acid until the excess of acid begins to volatilise; this solution is then diluted, and the separated silica filtered off. Ferric oxide is separated from alumina and titanitic acid in the filtrate by sodium thiosulphate (Chancel's method, cf. *infra*, p. 611). The alumina and titanitic acid are then precipitated together by boiling the solution; the precipitate is dissolved in hydrochloric acid, and the alumina precipitated by sodium hydroxide.

P. Kienlen<sup>3</sup> gives the following details for the analysis of bauxite, as the result of prolonged experience:—2.5 g. of very finely powdered bauxite are dried for eight hours at 100°, and then boiled with dilute sulphuric acid (1:1) until vapours of sulphuric acid begin to come off; the formation of crusts must be avoided during the evaporation, by thorough shaking. When perfectly cold, the residue of sulphates is transferred to 300 c.c. of cold water, care being taken that the temperature does not rise too high, as otherwise titanitic acid would be precipitated; 10 c.c. of hydrochloric acid are then added, and the mixture digested for six hours, with shaking. The separated silica acid is then filtered off; this may contain a very small quantity of alumina and traces of titanitic oxide. The solution and

<sup>1</sup> *Papier Zeit.*, 1904, 259.

<sup>2</sup> Jurisch, *Fabrikation der schwefelsauren Tonerde*, p. 45.

<sup>3</sup> Private communication, G. L.

washings are diluted to 500 c.c. The ignited and weighed crude silica is evaporated with three to four drops of dilute sulphuric acid and 2 c.c. of hydrofluoric acid, and the residue ignited; the loss in weight gives the amount of  $\text{SiO}_2$ . The residue can be taken as  $\text{Al}_2\text{O}_3$  without appreciable error; for very accurate work it should be fused with acid potassium sulphate, the melt dissolved in cold water acidified with sulphuric acid, the solution almost neutralised, diluted considerably, and the contained  $\text{TiO}_2$  precipitated by boiling for two hours.

The filtrate and washings from the initial precipitate of silica are made up to 500 c.c. Of this solution 200 c.c. (=1 g. bauxite) are neutralised with sodium carbonate until a slight precipitate is formed, which is redissolved by a little dilute sulphuric acid; the ferric oxide is reduced to the ferrous condition either by acid sodium sulphite, or by gaseous sulphur dioxide, the solution diluted to 400 or 450 c.c., and boiled for two hours, the water which evaporates being replaced by sulphurous acid solution. Under these conditions the whole of the titanic oxide separates free from iron; when cold the solution is made up to 500 c.c. and poured through a dry filter paper. The titanic oxide is washed with warm water containing ammonium chloride, the wash water being kept distinct from the first filtrate, then dried, strongly ignited, and weighed.

One hundred and twenty-five c.c. of this filtrate (=0.25 g. bauxite) are boiled till free from sulphur dioxide, a little pure zinc added, the solution diluted considerably and titrated with potassium permanganate solution after acidifying with sulphuric acid.

Alumina, ferric oxide, and titanic oxide are estimated together in 25 c.c. of the filtrate from the silica (=0.125 g. bauxite). A little fuming nitric acid and hydrochloric acid is added, the solution diluted, boiled, and precipitated with ammonia whilst boiling (cf. *infra*, p. 610); the precipitate is washed by decantation, dissolved in hydrochloric acid, the boiling solution reprecipitated by ammonia, and the precipitate thoroughly washed, ignited, and weighed. The  $\text{Al}_2\text{O}_3$  is calculated by subtracting the values found for  $\text{TiO}_2$  and  $\text{Fe}_2\text{O}_3$  as above from the total weight of oxides. Iron and alumina may also be separated by any of the ordinary methods.

To estimate the chemically combined water and the organic matter a separate sample is ignited for fifteen minutes on the blowpipe.

According to Baud,<sup>1</sup> corundum and titanic oxide remain in the residue insoluble in dilute sulphuric acid when the above method is used. To avoid this he dissolves 2 g. of the sample in sulphuric acid diluted with an equal volume of water, without boiling; the solution is filtered into a litre flask, the residue washed and dried, and fused with 1 to 2 g. of acid potassium sulphate for a few minutes. The melt is dissolved in

<sup>1</sup> *Chem. Centr.*, 1903, II., 967.

water and the filtrate added to that obtained by the original treatment with sulphuric acid. The silica is thus obtained perfectly pure. Titanium is estimated in the filtrate by means of its colour reaction with hydrogen peroxide. A solution containing a known amount of titanous acid dissolved in sulphuric acid serves for comparison; ferric sulphate is added to this until its colour is equal in intensity to that of the above filtrate, and finally 1 c.c. of hydrogen peroxide is added to each solution. Or the titanium may be titrated with potassium permanganate after reduction with zinc to  $Ti_2O_3$ .

Taurel<sup>1</sup> precipitates the titanium dioxide in a formic acid solution by means of sulphur dioxide. The method described by Lienau<sup>2</sup> and used in French bauxite works presents no essentially new features; his results show that the combined water of bauxite does not begin to come off below  $150^\circ$ , and that any loss of weight by drying at  $110^\circ$  is due to hygroscopic water.

#### CONTROL OF WORKING CONDITIONS. (*P. Kienlen.*)

**Residue.**—The residue from the treatment of bauxite with sodium carbonate or hydroxide solution contains the whole of the ferric oxide, part of the silica, all the titanium (as sodium titanate), and more or less soluble or insoluble compounds of sodium with alumina and silica. The contained ferric oxide, alumina, and soluble sodium compounds are generally estimated. Two g. of the residue are boiled with 3 c.c. of concentrated sulphuric acid and 3 c.c. of water until the red colour has disappeared, the solution slightly diluted, filtered, and made up to 100 c.c. The iron is estimated in 10 c.c. of the filtrate after reduction, by titration with potassium permanganate; the alumina and ferric oxide are precipitated together from 20 c.c. and weighed. The soluble alkali is estimated by boiling with ammonium chloride, the liberated ammonia being led into standard hydrochloric acid.<sup>3</sup> Air-dry residues contain from 3 to 4 per cent.  $Na_2O$ , and from 5 to 6 per cent.  $Al_2O_3$ .

**Aluminate Solution.**—If the manufacture is satisfactorily conducted this should contain 1 mol.  $Al_2O_3$  (102.2) to 1.75 to 1.8 mol.  $Na_2O$  (62.1). Strong liquors, ready for precipitation, have a sp. gr. of 1.32 to 1.35 (tested hot), and generally contain from 170 to 175 g.  $Na_2O$  per litre. Ten c.c. of this liquor are diluted to 100 c.c. and 10 c.c. of the dilute solution used for analysis. The sodium hydroxide is titrated with normal acid and phenolphthalein in boiling solution; the alumina is estimated gravimetrically by acidifying the solution with hydrochloric acid and precipitating with ammonia. Or the following method may be used

<sup>1</sup> *Ann. Chim. anal.* 1904, 9, 323.

<sup>2</sup> *Chem. Zeit.*, 1905, 29, 584; 1280.

<sup>3</sup> *Cf. Knoblauch, Z. anal. Chem.*, 1882, 21, 161.



10 c.c. of the dilute solution (= 1 c.c. original liquor) are just acidified with hydrochloric acid until the precipitated alumina is redissolved sodium acetate solution and free acetic acid added, and then 40 c.c. of an *N*/10 solution of sodium-ammonium phosphate (= 20.916 g. per litre) of which 1 c.c. corresponds to 0.00511 g.  $\text{Al}_2\text{O}_3$ ; the whole is heated to boiling, and titrated back with uranium acetate solution, without filtering.

A volumetric method of estimating sodium aluminate, using sulphuric acid and tropæolin OO, was suggested by Bayer, but according to Kienlen the method is of no value. This may be the case, but Lunge's method for the analysis of sodium aluminate (cf. *infra*), using phenolphthalein and methyl orange, permits of  $\text{Na}_2\text{O}$  and  $\text{Al}_2\text{O}_3$  being estimated in one operation much more simply than as described above, provided that the estimation is correctly carried out, according to the instructions.

**Filter-press Cakes.**—Twenty-five g. are taken for the estimation of soluble sodium, which is carried out as described above, by distilling with ammonium chloride and collecting the liberated ammonia in standard hydrochloric acid.

## FINISHED PRODUCTS

The following alumina preparations are technically important:—Aluminium sulphate, potassium, sodium, and ammonium alums, the hydroxide or anhydrous alumina, and sodium aluminate. The numerous other aluminium salts are less important as articles of commerce; they are chiefly used as mordants in dyeing and in calico-printing, and are largely prepared by the consumers themselves; they include aluminium acetate, thiocyanate, chloride (anhydrous and solutions), hypochlorite, sulphite, thiosulphate, chlorate, etc.

### I. ALUMINIUM SULPHATE<sup>1</sup>

**Qualitative Examination.**—In the course of the qualitative examination a residue is sometimes obtained, which is insoluble in water; it is generally found in quite negligible amount, and consists essentially of silica and of very small quantities of alumina and of calcium oxide.

In the soluble portion *Iron* is first tested for, best by warming with a little pure nitric acid, addition of potassium thiocyanate solution, and extraction with ether; a parallel test is carried out with distilled water. 0.1 c.c. of an iron solution containing 0.00001 g. Fe per 1 c.c. suffices to give a distinct rose colour to the ether, so that 1/1000 mg. of iron is easily detected.

<sup>1</sup> Except where otherwise stated, or where generally known facts are given, the following data are based essentially on the work of von Kéler and Lunge, *Z. angew. Chem.*, 1894, 7, 670.

Gallic acid solution may also be used for this purpose; traces of iron give a bluish-violet coloration, larger quantities give a bluish-black, ink-like colour.

*Copper* is detected by the usual reactions: addition of ammonia in excess gives a blue solution; potassium ferrocyanide gives a brownish-red precipitate, and a bright piece of iron is coloured red when placed in the solution. Kéler and Lunge were unable to find copper in any of the samples they examined.

*Lead.* Excess of ammonia is added to the alum solution and any ferric hydroxide which is separated filtered off; if the filtrate is blue, pure potassium cyanide is added until colourless, and the solution treated with sulphuretted hydrogen.

*Zinc* is often present, especially in products of French manufacture. To detect it, lead is first precipitated by dilute sulphuric acid, the filtrate treated with sodium hydroxide solution till the precipitate first formed redissolves, any ferric hydroxide filtered off, and the filtrate treated with sulphuretted hydrogen.

*Chromium* was not found in any of the commercial samples examined by Kéler and Lunge; it occurs, however, in some preparations of aluminium sulphate, especially in those manufactured from Irish bauxite. According to Marchal and Wiernik,<sup>1</sup> it may be detected by warming the solution under examination with a small quantity of freshly precipitated manganese dioxide; the latter is best prepared for this purpose by the interaction of manganese sulphate and potassium permanganate in equimolecular proportions. In presence of even extremely small quantities of chromium, a distinct yellow coloration is formed in the filtered solution, which is turned temporarily blue by hydrogen peroxide.

*Arsenic* is found in traces in most commercial samples; for its detection, cf. p. 362.

*Vanadium, Tungsten, and Titanium* are seldom present.

*Free Sulphuric Acid* is detected by extracting the thoroughly dried sample with absolute alcohol and testing the solution with litmus paper; a more convenient test is that with tincture of logwood made from one part of logwood extract, three parts of distilled water, and one part of alcohol. The violet colour of the tincture is turned to brownish-yellow. These two tests are not to be regarded as reliable in the case of small quantities of free acid; in such cases the quantitative methods (cf. p. 615) must be used.

*Calcium and Magnesium* were not detected by Kéler and Lunge in the soluble portions of any of the samples they examined; their presence would in any case be practically immaterial. *Sodium* was always present, but not *Potassium*.

<sup>1</sup> Z. angew. Chem., 1891, 4, 512.

**Quantitative Analysis.**—This is generally confined to the estimation of alumina; in some cases it is extended to the estimation of free acid and of iron. If, in an exceptional instance, sulphuric acid, alkalis, insoluble residue, zinc, etc., are to be determined, this is done by the ordinary methods of analysis.

1. *Alumina.* The usual method is to precipitate with ammonia in presence of ammonium chloride. Opinions differ as to the most advantageous way of carrying out the precipitation. It is well known that ammonia may dissolve freshly precipitated alumina to a slight extent, but that it is less liable to do so in presence of ammonium salts. According to Fresenius,<sup>1</sup> ammonium chloride and a slight excess of ammonia should be added to the solution, which is then heated for some time, until all the free ammonia has been driven off. L. Blum,<sup>2</sup> on the other hand, states that when a slight excess of ammonia is used the solution must only be boiled up for a moment, and then filtered. On comparing these methods, Lunge<sup>3</sup> found that of Blum decidedly the better, for the following reasons. In the first place, by prolonged boiling, as in other methods, the ammonium chloride is decomposed and alumina or iron is thereby dissolved; secondly, the precipitation and washing take less time by Blum's method, and the necessity of prolonged ignition on the blowpipe and repeated weighing is dispensed with, since the alumina is free from sulphuric acid when first precipitated.

Both methods were further examined by Kéler and Lunge (*loc. cit.*) under identical conditions, using one and the same solution of aluminium sulphate. Fresenius' method gave: 14.23, 14.23, 14.26: mean 14.24 per cent.  $\text{Al}_2\text{O}_3$ ; Blum's method: 14.65, 14.68, 14.61: mean 14.64 per cent.  $\text{Al}_2\text{O}_3$ . These results show that the prolonged boiling causes solution of some of the alumina in the acid liberated by the dissociation of the ammonium chloride; hence the results of the first method are too low, whilst the solubility of alumina in the slight excess of ammonia used in Blum's method may be neglected. Blum's method of precipitation is accordingly preferable.

Ferric oxide, silica, phosphoric acid, etc., are, of course, precipitated with the alumina; the amount of these in commercial aluminium sulphate is seldom of consequence. Debray<sup>4</sup> states that when zinc is present appreciable quantities may be precipitated with the alumina. In such a case the precipitate is dissolved, and the alumina and zinc are separated by the usual methods, *e.g.* by precipitating the zinc from acetic acid solution with sulphuretted hydrogen (*cf. infra*).

The following methods of analysis are recommended by Kretzschmar:<sup>5</sup>—

<sup>1</sup> Fresenius, *Quantitative Analysis*, 7th edition, vol. i., p. 192.

<sup>2</sup> *Z. anal. Chem.*, 1888, 27, 19.

<sup>4</sup> *Chem. Ind.*, 1882, 5, 153.

<sup>3</sup> *Z. angew. Chem.*, 1889, 12, 635.

<sup>5</sup> *Chem. Zeit.*, 1890, 14, 1223.

(1) *Gravimetric Estimation.* Ten g. of the alum or aluminium sulphate under examination are dissolved in water and diluted to 500 c.c.; 50 c.c. of this solution (= 1 g. substance) are treated with an excess of sodium phosphate and a little sodium acetate, and the precipitate dissolved in dilute hydrochloric acid. The solution is heated to boiling, a large excess of concentrated sodium thiosulphate solution added, and the mixture boiled until the precipitate settles out immediately after the vessel is removed from the wire-gauze; longer boiling must be avoided. The precipitate is filtered off, thoroughly washed with hot water, dried and ignited, finally with free admission of air. The weight of the aluminium phosphate, multiplied by 0.4185, gives the weight of alumina. The object of adding sodium thiosulphate is not to reduce any ferric oxide which may be present, but to obtain a precipitate which filters well and is easily washed. This method of estimation is very accurate.

(2) *Volumetric Estimation.* This is a much more rapid method. If the free acid in the solution of alumina consists only of acetic acid, the alumina may be precipitated by an excess of sodium phosphate; the excess of phosphoric acid, uncombined with alumina, may then be titrated with uranium acetate solution; the precipitate does not interfere with the titration. The alumina is calculated from the difference between the amount of phosphoric acid taken and the excess which remains in solution. This method in its original form cannot be recommended. The coloration with potassium ferrocyanide, which serves as the end-reaction, generally develops before the whole of the phosphoric acid is precipitated, and the results are thus rendered uncertain. Also the method necessitates a large number of titrations, whereby the economy in time becomes illusory; further, precipitated aluminium phosphate is appreciably soluble in solutions of ammonium salts.

By observing the following conditions, however, Kretzschmar states that very satisfactory results are obtained. No ammonium compounds must be present in the solution to be titrated, the excess of sodium phosphate must be added all at once and in the cold, and the solutions must be standardised by means of an analysed aluminium salt. The very convenient method of standardising uranium solution by means of calcium phosphate (iron-free superphosphate) is altogether unsuitable in this case.

The uranium solution is prepared in the usual way by dissolving uranium acetate (not nitrate) in the proportion of 35 g. per litre, and is standardised by sodium ammonium phosphate, the absolute purity of which must be checked by quantitative analysis (14.718 g. phosphate per litre); the uranium solution is diluted so that 1 c.c. corresponds to about 0.004 g.  $P_2O_5$ .

For the further standardisation 10 g. of pure, iron-free potassium alum are dissolved in water, and the free acid displaced by acetic acid by adding sodium acetate and a little acetic acid; the solution is then diluted to 500 c.c. Fifty c.c. of this solution are treated with 10 c.c. of the usual sodium acetate solution, and excess of sodium phosphate ( $\text{Na}_2\text{HPO}_4$ ) solution added, the strength of which has been previously determined by means of the titrated uranium solution. The solution is then heated to boiling and titrated with uranium solution. The titrations are repeated and the excess of phosphate reduced until finally only a few tenths of a c.c. of uranium solution are required to reach the end-point. The number of c.c. used is noted provisionally. As even the smallest and best formed crystals of alum enclose water, a gravimetric estimation of the contained alumina in the alum used must be made (p. 611) as a check on the standard solution.

When the percentage of alumina is calculated from both gravimetric and volumetric analyses, the results should not differ by more than 0.15 per cent. This can always be attained by having the same volume of liquid (viz. 60 to 70 c.c.) in standardising the uranium with sodium ammonium phosphate and in titrating the alum. The correct figure for the titre of the uranium solution is that given by the amount of alumina found by the gravimetric alumina estimation; the uranium titre is corrected accordingly.

In applying this method the tedious repetition of titrations may be avoided as follows:—The commercial aluminium salt under examination is first subjected to a preliminary titration with potassium hydroxide solution. A very little methyl orange is first added, and if a rose colour develops at all, the hydroxide is added till the colour disappears; phenolphthalein is then added, and the solution titrated until the red colour appears. If the strength of the alkali is calculated and expressed in terms of alumina, the approximate percentage of alumina can be obtained by subtracting the number of c.c. used for the titration with methyl orange, which corresponds to the free acid, from the total volume of potassium hydroxide used. The volume of uranium solution to be added in titrating the phosphoric acid is thus known within about 2 c.c., and hence with a little practice one titration of the sample should suffice.

A solution of ammonium alum is freed from ammonia (except for a slight harmless residue) by heating with a few small pieces of sodium hydroxide. The following will serve as an example of the method of analysis, according to Kretzschmar's method, of a very impure aluminium sulphate containing iron: 5 g. of the sample are dissolved, and made up to 500 c.c.; the free acid in 50 c.c. is estimated by potassium hydroxide and methyl orange, and the approximate amount of alumina by further titration after addition of phenolphthalein. Another 50 c.c.

are boiled with a few drops of hydrochloric acid containing bromine; when cold the free acid in the solution is displaced by acetic acid, sodium phosphate solution added, and the alumina estimated by a single titration with uranium acetate. Iron is estimated in another 50 c.c. by reduction with zinc and dilute sulphuric acid and titration with potassium permanganate; if an estimation of the ferrous iron is required, it may be determined by titration with potassium permanganate in 50 c.c. of the original solution; but this method is not generally sufficiently accurate (cf. *infra*). By subtracting the ferric oxide from the alumina found by the uranium titration, the actual percentage of alumina is obtained. It is advantageous to convert aluminium sulphite solutions into aluminium sulphate by treatment with a little bromine with the usual precautions.

14.5 per cent. of  $\text{Al}_2\text{O}_3$  is generally guaranteed in commercial aluminium sulphate. In thirteen commercial samples examined by Kéler and Lunge the contents varied little from 15 per cent.; one sample contained 13.81 per cent., another 16 per cent., and a third 17.48 per cent.

According to Gyzander<sup>1</sup> the sulphuric acid in aluminium sulphate can be accurately estimated by titration with sodium hydroxide solution, provided this reagent is free from carbonate and from alumina and is not stronger than  $\frac{1}{3}$  normal; stronger alkali causes the formation of basic salts. He recommends the use of a standard solution containing 11.65 g. NaOH per litre; using 0.5 g. aluminium sulphate for analysis, this indicates 1 per cent.  $\text{Al}_2\text{O}_3$  per c.c.; as an alternative, a more dilute alkali can be used and adjusted to indicate percentages of  $\text{Al}_2(\text{SO}_4)_3$ . Standard sulphuric acid solutions corresponding to the above alkalis are required. To carry out the titration 10 g. of the sample are dissolved in hot water, filtered, the residue washed, and the filtrate diluted to 1000 c.c.; 50 c.c. of this solution (=0.5 g. substance) are used for each titration. Methyl orange, phenolphthalein, and 2 c.c. of the standard sulphuric acid are added, and the standard alkali run in, drop by drop, with continual stirring, until the red colour of the methyl orange changes to orange (not to yellow). If the sulphate is neutral, exactly 2 c.c. of alkali are necessary; basic alums require less, acid alums more. The burette is then filled up again, and alkali run in, somewhat more quickly than before, until the red tint due to the phenolphthalein is just permanent. The number of c.c. used in the second titration gives the percentage of  $\text{Al}_2\text{O}_3$  directly, or multiplied by 3.33, the percentage of  $\text{Al}_2(\text{SO}_4)_3$ . The end-point is sharpest at 30°. Towards the end of the titration a rose-coloured phenolphthalein alumina lake is formed, which renders the recognition of the end-point more difficult; the addition of a little more methyl orange inhibits this effect. A basic alum should

<sup>1</sup> *Chem. News*, 1901, 84, 296; 306.

first be neutralised with sulphuric acid, to obtain accurate results. This method of estimating the free acid with methyl orange is accurate to within 0.2 per cent. Alums containing zinc cannot be titrated in this way; the zinc must first be precipitated with sulphuretted hydrogen, and iron, which invariably accompanies the zinc, must be estimated separately. This point must also be observed in the analysis of bauxite, as ferric oxide behaves in the same way as alumina during the titration, and the amount present must therefore be deducted. The ferrous sulphate must be estimated by titration with potassium permanganate, and the ferrous and ferric sulphates together in a separate sample, by reduction with sulphur dioxide and subsequent titration with potassium permanganate.

S. E. Moody<sup>1</sup> has devised a method for the determination of the free acid in aluminium sulphate and in alums based on the decomposition effected by means of a mixture of potassium iodide and iodate. The sulphuric acid, in combination with aluminium, iron, zinc, and ammonium, liberates one gram molecule of iodine for each gram molecule of sulphuric acid present. The liberated iodine is titrated with sodium thiosulphate, and the free sulphuric acid arrived at by deducting that corresponding to the above bases, as separately determined, from the total acid found. The accumulative small errors that are unavoidable in all the estimations involved must render the method somewhat uncertain.

2. *Iron.* Since in most cases the amount of iron in aluminium sulphate is extremely small, a gravimetric separation from alumina is out of the question. Titration with permanganate is also often unsuitable; even if 50 g. of the aluminium sulphate are taken and  $N/100$  permanganate used, the results are far from concordant.

The colorimetric method of determination with potassium thiocyanate is, however, applicable; it was first suggested by Herapath, and subsequently worked out and improved by Tatlock and by Kéler and Lunge,<sup>2</sup> and described in its final form by Lunge in 1896.<sup>3</sup> The method is given in detail under "Sulphuric Acid" (p. 381). The solution to be tested (*cf.* p. 382) is made up by dissolving 1 to 2 g. of aluminium sulphate in a little water, exactly 1 c.c. of iron-free nitric acid added, the solution warmed for a few minutes to oxidise all the iron to the ferric condition, cooled and diluted to 50 c.c.; this solution is then transferred to one of the colorimeter cylinders for comparison with the titrated iron-alum solution.

If it be desired to estimate both ferrous and ferric iron, the total iron is estimated in one sample as described, and a second sample is dissolved in air-free, distilled water in an atmosphere of carbon

<sup>1</sup> *Z. anorg. Chem.*, 1907, **52**, 286; *J. Soc. Chem. Ind.*, 1907, **26**, 200.

<sup>2</sup> *Z. angew. Chem.*, 1894, **7**, 670.

<sup>3</sup> *Ibid.*, 1896, **9**, 3.

dioxide, and the ferric iron estimated colorimetrically without addition of nitric acid.

In thirteen samples of commercial aluminium sulphate Kéler and Lunge found:—

	Total iron.	Ferric oxide.	Ferrous oxide.	
Minimum	0.00050	0.00027	0.00023	per cent.
Maximum	0.00524	0.00406	0.00118	per cent.

As the result of a series of experiments carried out on a large scale by Kéler and Lunge in conjunction with Fischli, it was found that the value and purity of the shades obtained in turkey-red dyeing diminishes very markedly with an increase in the percentage of iron. Aluminium sulphate for use in turkey-red dyeing should not contain more than 0.001 per cent. of total iron. There is no object in preparing a purer product, as the influence on the dye is practically negligible if the proportion of iron does not exceed this value; if, however, a greater quantity of iron is present it has a decidedly injurious effect. The stage of oxidation of the iron is also of importance; ferrous salts are less harmful than ferric. The presence of zinc, which however seldom occurs in commercial alumina, has also an injurious influence on the colour. In selecting aluminium sulphate for use in turkey-red dyeing, that which is poorest in iron and free from zinc should therefore be chosen.

Experiments with printed woollen goods showed, on the other hand, that the quality of both red and rose colours were unaffected by any of the samples used which contained up to 0.00534 per cent. of iron; nor could any difference be detected, even on using an artificially prepared sample containing 1 per cent. of iron, an extreme which never occurs in practice. This is no doubt due to the fact that the amount of mordant left on the fibre in printing is very small. Similarly the thirteen commercial samples were without effect on buckthorn-yellow, a dye which is very sensitive towards iron, so that in this case also contamination of the aluminium sulphate by iron up to 0.005 per cent. has no injurious action.

As regards paper manufacture, a content of iron up to 0.15 per cent. has no effect in sizing good quality writing-paper;<sup>1</sup> if the iron is all in the ferrous condition, which is seldom the case, it may be present up to 0.3 per cent. without affecting the quality of the paper. Products containing from 0.3 to 0.5 per cent. of iron can only be used for poor quality papers.

3. *Free Acid.* The presence of free acid in aluminium sulphate used in dyeing, printing, and in sizing paper is immaterial, since it is always evaporated with sodium carbonate or with acetates when used for these

<sup>1</sup> *Papier-Zeit.*, 1891, 2327.



purposes. The estimation of free acid may in some cases, however, be of importance.

The various methods for the determination of the free acid have been exhaustively discussed by Beilstein and Grosset<sup>1</sup> and more recently by Kéler and Lunge (*loc. cit.*). The latter found from 0.53 to 1.05 per cent. of free sulphuric acid in the thirteen commercial samples they examined; they concluded that nearly all the methods which have been suggested for the estimation are quite inaccurate, with the exception of that worked out by Beilstein and Grosset.

This method depends on the fact that when neutral ammonium sulphate is added to aluminium sulphate, the latter is almost completely precipitated as ammonium alum, and the whole of the free sulphuric acid remains in solution. The remaining alum and the excess of ammonium sulphate are precipitated by alcohol, so that the alcoholic solution contains only a little ammonium sulphate in addition to the free sulphuric acid.

To carry out the determination according to Beilstein and Grosset's directions, 1 g. of the sample, or 2 g. in the case of samples poor in acid, are dissolved in 5 c.c. of water, 5 c.c. of a cold, saturated ammonium sulphate solution added, and the mixture allowed to stand with frequent shaking for a quarter of an hour; it is then precipitated by 50 c.c. of 95 per cent. alcohol, the precipitate filtered off and washed with 50 c.c. of 90 per cent. alcohol; the filtrate is evaporated on the water-bath, the residue taken up with water, and this solution titrated with *N*/10 alkali and phenolphthalein.

Kéler and Lunge investigated this method in the case of a sample of aluminium sulphate which had been proved by careful complete analysis to contain 0.92 per cent. of free sulphuric acid; 5 g. of substance were taken for the estimation instead of 2 g., so as to reduce the errors of the analysis. The results obtained were: 0.97, 0.98, 1.02, 1.00, 1.02 per cent., thus all slightly, on the average about 0.1 per cent., too high. For practical purposes this may be considered sufficiently accurate, and since the method is easily carried out, it is certainly to be recommended before other methods, for technical purposes; a more rapid method is nevertheless desirable.

Direct titration with litmus, methyl orange, tropæolin OO, or other indicators, gives quite unreliable results, and this is also the case with the titration of the alcoholic extract.

A. H. White<sup>2</sup> found that if neutral potassium sodium tartrate (Rochelle salt) is added to a solution of alum, and this solution titrated with barium hydroxide and phenolphthalein, the amount of the hydroxide neutralised indicates the free sulphuric acid plus that combined with alumina, but not that combined with the sodium or potas-

<sup>1</sup> *Z. anal. Chem.*, 1890, 29, 73.

<sup>2</sup> *J. Amer. Chem. Soc.*, 1902, 24, 457.

sium. If a second portion of the alum solution is evaporated to dryness, the residue dissolved in neutral sodium citrate and titrated with barium hydroxide, the quantity used is less than in the former case by an amount corresponding to one-third of the alumina. From these two titrations both the alumina and the sulphuric acid can be calculated, irrespective of whether the alum is basic or acid; in the latter case the amount of free acid is obtained. Commercial aluminium sulphate may contain free acid whilst solid, which disappears on solution owing to combination with basic salt. This free acid may be estimated by dissolving the sulphate directly in sodium citrate, and titrating immediately with barium hydroxide. The results thus obtained agree well with those got by Beilstein and Grosset's method, but an alum of this character may possibly not contain more acid than is required to form the normal sulphate  $\text{Al}_2(\text{SO}_4)_3$ .

4. *Other Constituents.* Of the thirteen commercial samples examined by Kéler and Lunge only one (of French manufacture) contained any zinc, viz., 0.00156 per cent. Sodium (as  $\text{Na}_2\text{O}$ ) was present to the extent of from 0.17 to 0.205 per cent., and the insoluble residue amounted to from 0.15 to 0.43 per cent.; the two latter constituents may be regarded as immaterial. Those samples in which iron was high also contained more insoluble residue; this is probably connected with less careful manufacture.

Zinc has, as stated, a decidedly injurious action in turkey-red dyeing, and should therefore be estimated quantitatively whenever present. The simplest method is to add sufficient barium acetate to the aluminium sulphate solution to precipitate the whole of the sulphuric acid, and then to estimate the zinc in the filtrate as sulphide.

## II. POTASSIUM, SODIUM, AND AMMONIUM ALUMS

The examination of these salts is conducted exactly as in the case of aluminium sulphate; the estimation of the ammonia and of the alkali is carried out by the ordinary methods.

In most cases the purchaser is content to judge the product by its external appearance, but this is, of course, no guide as to the presence of iron in moderately small quantity; the latter may be estimated when necessary as described on p. 614.

## III. SODIUM ALUMINATE

This preparation is used in dyeing, printing, in preparing lakes, and sometimes in sizing paper; also in the manufacture of milk-glass, for hardening bricks, and in soapmaking. The analysis is generally limited to the estimation of sodium and of alumina; impurities such as insoluble matter, silica, and iron are sometimes determined.

1. *Sodium* ( $\text{Na}_2\text{O}$ ) *and Alumina*. This estimation is best effected by Lunge's<sup>1</sup> titration method, which is based on the following observations:—

When a hot solution of sodium aluminate, or of sodium hydroxide containing alumina (such as Caustic "Bottoms," *cf.* p. 441) is titrated with acid in presence of litmus, or better, of phenolphthalein, the end-reaction occurs as soon as the whole of the alkali is neutralised by the acid, and the alumina begins to be precipitated. When methyl orange or cochineal, which is not so good, is used as indicator, the end-reaction does not occur until the precipitated alumina is redissolved, a condition which corresponds to the formation of the compound  $\text{Al}_2(\text{SO}_4)_3 = \text{Al}_2\text{O}_3 \cdot 3\text{SO}_3$ . The aluminium hydroxide, either in a colloidal condition, or suspended in the liquid, dissolves very slowly in the cold, but solution is rapid and certain at about  $30^\circ$ .

Cross and Bevan<sup>2</sup> have expressed the view that the end-reaction corresponds rather with the formation of a compound  $2\text{Al}_2\text{O}_3 \cdot 5\text{SO}_3$  than with that given above, but Lunge<sup>3</sup> regards this as incorrect.

For the estimation, 20 g. of sodium aluminate are dissolved in water and the solution made up to 100 c.c. Ten c.c. (= 0.2 g. substance) are titrated hot with phenolphthalein and *N*/5 hydrochloric acid until the red colour disappears; the influence of any traces of carbonic acid which may be present is rendered practically negligible by titrating hot. The amount of acid used is read off, not more than one drop of methyl orange added to the solution, and the titration with the hydrochloric acid continued. The introduction of the cold acid will generally bring down the temperature to from  $30^\circ$  to  $37^\circ$ ; if necessary, the solution must be cooled, or if too cold the vessel should be left to stand in a warm place. The titration is continued until the methyl orange is turned permanently red, and the alumina is then calculated by difference. The silica present, which is always in only extremely small amount, does not interfere, since the indicators have no action upon it.

*Example of calculation.* 10 c.c. of the sodium aluminate solution (corresponding to 0.2 g. substance) required 8.5 c.c. of acid to decolorise the phenolphthalein, and a total of 23.85 c.c. to permanently colour the methyl orange red;  $23.85 - 8.50 = 15.35$  c.c. therefore correspond to the alumina. 1 c.c. *N*/5 hydrochloric acid is equivalent to 0.00621 g.  $\text{Na}_2\text{O}$  and to 0.003407 g.  $\text{Al}_2\text{O}_3$ . The percentage of  $\text{Na}_2\text{O}$  is accordingly = 26.35, and that of  $\text{Al}_2\text{O}_3$  = 26.09.

2. *The Insoluble Residue* is estimated in 10 or 20 g. of substance as in the analysis of sodium carbonate (*cf.* p. 457); the hardened filter paper made by Schleicher and Schüll, or some other good quality paper, should be used for the filtration.

<sup>1</sup> *Z. angew. Chem.*, 1890, 3, 227, 293.

<sup>2</sup> *J. Soc. Chem. Ind.*, 1889, 8, 253; 1891, 10, 202.

<sup>3</sup> *Z. angew. Chem.*, 1890, 3, 299.

3. *Silica* is estimated by evaporation with hydrochloric acid and washing in the usual way. Bayer states<sup>1</sup> that sodium aluminate solution is only capable of holding a few tenths per cent. of silica in solution, just as conversely water-glass solution can only take up traces of alumina.

4. *Traces of Iron* are detected as described on p. 614.

#### IV. ALUMINA

*Alumina* comes into the market as the hydroxide which contains from 64 to 65 per cent. of  $\text{Al}_2\text{O}_3$ , and anhydrous, containing nearly 99 per cent. of  $\text{Al}_2\text{O}_3$ ; the latter is chiefly used for the manufacture of aluminium.

The usual impurities consist of small quantities of silica and of sodium carbonate, which are detrimental in the electrolytic preparation of aluminium; traces of iron taken up in the course of manufacture may also be present.

For analysis the substance is dissolved in hydrochloric acid, the *Alumina* estimated as on p. 610, and the *Silica* as on p. 605. *Sodium* is determined in the filtrate from the alumina, which is carefully evaporated, the dry residue gently heated to drive off ammonium chloride, but not strongly enough to volatilise the sodium chloride, and the latter weighed. *Iron* is estimated as on p. 614.

According to P. Kienlen, aluminium hydroxide is generally guaranteed to contain 60 per cent. of  $\text{Al}_2\text{O}_3$ ; he estimates the silica as usual, and checks the determination by evaporation with hydrofluoric acid (p. 606). "*Combined Sodium*," which is always present, he estimates as follows: 5.305 g. of substance are heated to a moderate red heat and then digested with water; an excess of normal sulphuric acid is added, the solution boiled, and titrated back with normal sodium hydroxide. This gives the "*Total Sodium*." The "*Soluble Sodium*" is estimated by boiling 5.305 g. of substance with 100 c.c. of water and titrating with normal sulphuric acid and phenolphthalein; 1 c.c. normal acid = 1 per cent.  $\text{Na}_2\text{CO}_3$ . The difference between these two estimations gives the "*combined sodium*." The total sodium may also be estimated by boiling with ammonium chloride (*cf.* p. 607). The *Loss on Ignition* ( $\text{H}_2\text{O} + \text{CO}_2$ ) is determined by igniting for fifteen minutes on the blowpipe, and the alumina is estimated either by difference or by precipitation with ammonia.

Good aluminium hydroxide contains on an average 63 per cent.  $\text{Al}_2\text{O}_3$ , 0.90 per cent.  $\text{SiO}_2$ , 0.003 per cent. Fe, 0.90 per cent.  $\text{Na}_2\text{CO}_3$ , 0.80 per cent.  $\text{Na}_2\text{O}$  (combined) and 34.40 per cent. loss on ignition. Preparations manufactured by Bayer's process (spontaneous decomposition of aluminate solutions) contain only 0.15 per cent.  $\text{SiO}_2$ .

<sup>1</sup> *Z. angew. Chem.*, 1891, 4, 512.

Kierlen estimates silica in *Calcined* (metallurgical) *alumina* by fusing with acid potassium sulphate and extracting the melt with water; the solution is filtered, the residue fused with sodium carbonate, dissolved, evaporated with acid, and the silica filtered off, weighed, and volatilised by hydrofluoric acid. To estimate the sodium ( $\text{Na}_2\text{O}$ ) 1 g. of the sample is very finely powdered and mixed with 1 g. of ammonium chloride and 8 g. of calcium carbonate, and the mixture ignited in a platinum crucible, at first gently and then strongly for thirty minutes. When cold, the mass is macerated with a little water, rinsed into a flask, and the residue thoroughly washed. The filtrate is treated cold with ammonium carbonate solution, stirred until the calcium carbonate has become granular, filtered, and the filtrate evaporated in a platinum dish and finally on the water-bath. The residue is ignited to drive off ammonium salts, dissolved in water, a few drops of ammonium carbonate solution added, any precipitate that forms filtered off, the resulting solution again evaporated as before, and the residue ignited and weighed. It is advisable to make a control test, with the reagents used, for the presence of sodium chloride. The loss on ignition is also determined; the alumina is generally taken by difference.

Good metallurgical alumina contains 98.40 per cent.  $\text{Al}_2\text{O}_3$ , 0.03 to 0.25 per cent.  $\text{SiO}_2$ , 0.10 per cent.  $\text{Fe}_2\text{O}_3$ , 0.10 to 0.15 per cent.  $\text{Na}_2\text{O}$ , and 0.20 to 0.80 per cent.  $\text{H}_2\text{O}$ .

#### V. ALUMINIUM SALTS USED IN DYEING, ETC. (ACETATE, THIOCYANATE, ETC.)

These salts, which are enumerated on p. 608, may be examined either as to their content of alumina (*cf.* p. 610) or as to their acid constituents; the latter are estimated by methods which are either generally known, or which are described in other sections: *e.g.*, thiocyanic acid by precipitation as copper thiocyanate (p. 565), hypochlorous acid as described on p. 510, chloric acid as on p. 511, thiosulphuric acid by iodimetry, p. 117, etc.

As a rule these estimations are omitted, because the analytical data give the manufacturer but little information as to the practical value of the sample. It is preferable to carry out a practical test, either in dyeing or in printing, and to compare the result with that obtained with a "standard" preparation.

#### LITERATURE

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## GLASS

By Professor E. ADAM, The Art-trade School of the Royal Austrian Museum of Art and Industry, Vienna. English translation revised by W. Thomason.

GLASS in the broader sense of the word is usually understood to be a complex of silicates produced by fusion, of an amorphous, transparent or opaque nature, which in some cases may contain dissolved borates, phosphates, fluorides, metals, metalloids, and sulphides. All glasses of technical importance are characterised by becoming liquid at high temperatures and tough and viscous on slowly cooling; they can be moulded to a definite form before solidification, and are more or less resistant to the action of the atmosphere, water, and chemical agents. Experience has shown that only silicates of the complexity of at least double silicates possess these properties, and that the oxides of the alkaline earths or of aluminium, zinc, and heavy metals must form a constituent part of such glass in addition to the oxides of the alkalis; the technical glasses are accordingly mostly alkali-lime or alkali-lead silicates. Schott<sup>1</sup> has recently succeeded in producing boro-silicate glass entirely free from alkali; it is easily workable and resistant, and in consequence of its being less sensitive to sudden changes of temperature than alkali-lime or lead glass, it is more suitable for many purposes.

### I. RAW MATERIALS

The raw materials employed in the manufacture of glass may be classified as follows:—

- |                            |                                      |
|----------------------------|--------------------------------------|
| 1. Silica and Silicates.   | 5. Lead oxide.                       |
| 2. Boric acid and Borates. | 6. Other Metallic oxides and Fluxes. |
| 3. Alkaline Fluxes.        | 7. Decolorising agents.              |
| 4. Lime.                   | 8. Colouring agents.                 |

### I. SILICA AND SILICATES

Silica is introduced into the mixture of raw materials, "the frit," as sand, quartz, or flint, and in many cases in the form of a natural silicate.

<sup>1</sup> *Ann. Physik.*, 1889, 38, 453.

**Sand** is the most widely used form of silica. To produce a perfectly colourless glass it must be as free as possible from iron; very pure sand contains from 0.005 to 0.015 per cent. of ferric oxide.<sup>1</sup> A small quantity of alumina or of alkali is rather beneficial than harmful. Alumina<sup>2</sup> stops the tendency to devitrification in the furnace and in the working of the glass in the blowpipe; it also effects an economy of material. Ferruginous sand is of value in the manufacture of green or brown bottle glass. The size of the grain is of importance, since fine grain sands are more readily attacked by the fluxes than coarse grain.

The sand used in the manufacture of ordinary window glass and of bottle glass is usually obtained in the vicinity of the works. Belgian sand is almost invariably used for the manufacture of plate glass; its technical value is judged by the colour on ignition and by chemical examination.

The chief Austrian and German glass-works use sand from Hohenboka for the manufacture of fine colourless glass; this consists of quartz grains about  $\frac{1}{2}$  mm. in diameter, and is separated on the spot by washing, from the small quantities of mica and clay with which it is associated; the washed sand contains approximately 99.7 per cent. of silica and only traces of iron.

Sand from Martinroda, which is employed in Thuringia in the manufacture of lamp glasses, contains 3.8 per cent. of alumina and 2.7 per cent. of potassium oxide (Weber).

A rough test of the suitability of a sand for glassmaking is effected by strongly heating it in a glass furnace; if the sand contains an appreciable quantity of iron, it will appear grey after the heating.

An exact estimation can only be obtained by the quantitative determination of the contained bases. For this purpose the sample of sand is very finely powdered in an agate mortar and 5 g. treated either in a weighed platinum basin or in a capacious crucible with hydrofluoric acid and allowed to stand covered with a platinum lid, with frequent stirring, until no more gritty particles are observable. The reaction can be conducted either at the ordinary temperature or upon a gently heated water-bath; in the latter case the crucible lid must fit tightly and the evaporated hydrofluoric acid must be replaced as required. The decomposition even upon heating takes considerable time on account of the slow solubility of crystalline silica in hydrofluoric acid. When solution is complete, the lid is removed, the contents of the crucible evaporated to dryness upon the water-bath, allowed to cool, and ten to twenty drops of sulphuric acid (1 : 1) added; the residue is then carefully taken to dryness upon an asbestos gauze, and finally gently ignited and weighed. It is then dissolved in hot

<sup>1</sup> Lecrenier, *Bull. Soc. Chim.*, 1904, 18, 404.

<sup>2</sup> Weber, *Verhdl. d. Ver. z. Bef. d. Gewerbeß.*, 1888, 152; Schott, *Sprechsaal*, 1888, 125.

water, hydrochloric acid added, and the contained sulphuric acid estimated by barium chloride; the weight of the bases in the sand is found by difference. Should the latter be present in considerable quantity, they can be separated in the hydrochloric acid solution and determined.

If it is only required to estimate the contained iron, the weighed residue is dissolved in dilute sulphuric acid and the iron in this solution reduced by chemically pure zinc and determined by standard potassium permanganate solution.

The amount of silica is found by difference if the bases have been quantitatively determined. For a direct determination, 1 g. of the finely powdered sand is fused with sodium-potassium carbonate and the separation of the silica effected as in the analysis of glass (*cf.* p. 644).

To decide whether a sand can be freed from the accompanying impurities by means of washing, a fair-sized sample is stirred up in a porcelain basin with a considerable amount of water; the turbid washings are rejected and the washing continued until the decanted water remains clear. By a determination of the bases or of the iron contained in the washed and in the unwashed sand the extent of the purification effected can be gauged.

**Quartz** is less often employed in the manufacture of glass than sand, since its application always entails a previous sorting, roasting, quenching, and disintegration. The determination of its value and its examination are conducted in the same way as with sand. It is advantageous in the analysis of quartz to heat the pieces in a fire-clay crucible and quench in cold water before powdering, as the disintegration is thus made easier and a better average sample is obtained.

**Flint** occurs in irregular pieces of varying size in the chalk formation, and is mostly coloured yellow by organic matter, but on heating becomes white. It is a very pure form of silica, but since it is difficult to powder and its price higher than that of sand, its application is limited.

**Natural Silicates.**—Many naturally occurring silicates, such as granite, trachyte, basalt, obsidian, pumice, lava, and argillaceous marl, are extensively used in the production of various kinds of glass. When comparatively cheap, they form an advantageous substitute not only for sand and quartz but also for alkali and lime, on account of their content of these materials. Owing to the considerable quantity of alumina and iron which they contain, their application is strictly confined to the production of green or brown bottle glass; the estimation of their constituents is carried out according to the methods given for the analysis of glass (p. 641).



## 2. BORIC ACID AND BORATES

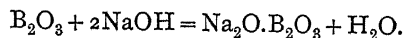
Boric acid is used in the production of coloured glass, and in the manufacture of the glass compositions known as "strass" and "enamel"; it is now also employed in the preparation of those varieties of glass the great resistance of which to changes of temperature render them suitable for lamp glasses, laboratory utensils, etc. It is used as crystallised boric acid, as borax, or in the form of naturally occurring borates, if their chemical composition is suitable.

**Boric acid.**—This occurs in commerce in different degrees of purity, and contains, besides hygroscopic water, often considerable quantities of impurities such as alkali sulphates and chlorides, ferric oxide, alumina, lime, magnesia, sulphuric acid, silica, and organic matter.<sup>1</sup>

For the examination of crude boric acid for technical purposes it is sometimes sufficient to determine the hygroscopic water by drying for two hours at 50° and then over sulphuric acid for twelve hours, and also the residue insoluble in alcohol; the difference gives approximately the weight of boric acid.

More exact results are obtained according to Zschimmer<sup>2</sup> by titrating the boric acid with standard barium hydroxide solution in the presence of a large excess of glycerol, using phenolphthalein as indicator.

An alternative volumetric method for the estimation of boric acid is that of Cleveland Jones.<sup>3</sup> Litmus is added to the solution to be examined, which is then made distinctly acid by hydrochloric acid and 5 c.c. of a 10 per cent. solution of barium chloride added to precipitate free carbonic acid. Also, about 10 c.c. of a 25 per cent. solution of potassium iodide is mixed with an equal volume of a saturated solution of potassium iodate to which starch solution is added, and the colour exactly destroyed by sodium thiosulphate solution. This iodide-iodate solution is then added to the boric acid solution, the whole decolorised again by thiosulphate solution, a few drops of phenolphthalein solution added and titrated with standard sodium hydroxide solution to a distinct red coloration. The colour is then destroyed by the addition of about 1 g. of mannitol, and standard alkali again added until a faint red coloration is formed, which remains permanent on the further addition of mannitol. The quantity of boric acid is calculated from the volume of standard alkali used, according to the following equation:—



It is most advantageous to work in a cold solution the volume of

<sup>1</sup> Cf. Dammer, *Anorganische Chemie*, vol. iii., p. 61.

<sup>2</sup> *Chem. Zeit.*, 1901, 25, 67; cf. also, Thomson, *J. Soc. Chem. Ind.*, 1893, 12, 433.

<sup>3</sup> *Z. anorg. Chem.*, 1899, 20, 212; 1899, 21, 109.

which is less than 50 c.c. Silica and hydrofluoric acid have no influence upon the reaction.

For the complete examination of crude boric acid 2 to 3 g. are dissolved in hot water, filtered from any insoluble residue, nitric acid added to the filtrate, and the silica separated from one-half of this solution; silver nitrate is added to the other half of the solution to precipitate the chlorine and then barium nitrate to precipitate the sulphuric acid. A second sample is evaporated with hydrofluoric acid and a little sulphuric acid to dryness, the residue dissolved in dilute hydrochloric acid, and the contained ferric oxide, alumina, calcium, magnesium, potassium, and sodium separated and estimated in the usual way.

Should the boric acid contain ammonium salts, which is frequently the case, a separate quantity is heated with sodium hydroxide solution, the evolved gas absorbed in standard sulphuric acid solution and the excess of acid titrated back with standard alkali. The hygroscopic water is estimated as described above and the boric acid calculated by difference.

**Borax** is usually employed as refined borax, since the cheaper crude preparations contain considerable quantities of insoluble constituents in addition to chlorides and sulphates. The examination is carried out according to the method given for boric acid and for the natural borates.

**Natural Borates.**—Among the many naturally occurring borates only calcium borate or borocalcite ( $\text{Ca}_2\text{B}_6\text{O}_{11} \cdot 4\text{H}_2\text{O}$  or  $\text{CaB}_4\text{O}_7 \cdot 6\text{H}_2\text{O}$ ) and boronatrocalcite ( $\text{NaCaB}_5\text{O}_9 \cdot 8\text{H}_2\text{O}$ ) are of importance for the glass industry; boracite ( $2\text{Mg}_3\text{B}_8\text{O}_{15} \cdot \text{MgCl}_2$ ) is unsuitable on account of its large content of magnesium chloride.

The boric acid in natural borates is determined either by difference or a sample is fused with from four to six times its weight of potassium carbonate, the fused mass extracted with water, and the boric acid separated as potassium borofluoride.

Several volumetric methods have been recommended for the determination of boric acid in alkali and alkali-earth borates. According to that of Jörgensen,<sup>1</sup> modified by Hönig and Spitz,<sup>2</sup> for the estimation of boric acid in alkaline borates, 30 g. of the salt are dissolved in water and the solution made up to 1 litre. The alkali is estimated in 50 c.c. of the clear solution by means of  $N/2$  acid and methyl orange. To the solution thus obtained, which is neutral to methyl orange and which contains all the boric acid in the free state, two to three drops of phenolphthalein and 50 c.c. of glycerol are added and the whole titrated with  $N/2$  alkali until a red coloration is produced. Glycerol in portions of 10 c.c. at a time and the standard alkali are then further added so long as the violet coloration is no longer destroyed by a fresh addition of glycerol.

<sup>1</sup> *Z. angew. Chem.*, 1897, 10, 5.

<sup>2</sup> *Ibid.*, 1896, 9, 549; *Z. anal. Chem.*, 1903, 42, 119.

Each c.c. of  $N/2$  alkali used corresponds to 0.0175 g.  $B_2O_3$ , according to the equation given above.

For the estimation of borates insoluble in water such as boronatrocalcite, boracite, borocalcite, etc., 2 g. of the sample are boiled with 50 c.c. of normal acid in a flask, attached to a reflux condenser. After the solution has cooled the condenser tube is washed out, the excess of acid neutralised with alkali, and the determination proceeded with as described above.

A critical summary of the methods proposed for the estimation of boric acid has been given by M. Schaak,<sup>1</sup> who recommends the following modification for natural borates. The sample is dissolved in an excess of dilute hydrochloric acid by heating in a flask attached to a reflux condenser, the solution made up to a definite volume, filtered, and 100 c.c. of the filtrate (2 to 4 g. of substance) almost neutralised with alkali, after addition of methyl orange. From 2 to 3 g. of barium carbonate are then added to complete the neutralisation and to precipitate the salts of iron and aluminium, the presence of which interferes with the subsequent titration. The whole is warmed on the water-bath for half an hour, allowed to cool, filtered, the filtrate made up to 200 c.c., one-third of its volume of neutral glycerol added, and titrated with standard sodium hydroxide solution, free from carbonate, using phenolphthalein as indicator. The method is both rapid and convenient. (Thomason.)

J. Wolff<sup>2</sup> has modified Hönig and Spitz's method by substituting ferric sodium salicylate as indicator in place of methyl orange, in the first neutralisation. The salicylate is prepared by dissolving freshly precipitated ferric hydroxide in a concentrated, neutral sodium salicylate solution by heating for a short time at 80°. For the estimation of boric acid in borax a solution is prepared with air-free water to which 0.5 to 1 c.c. of the indicator and either sulphuric or hydrochloric acid diluted with an equal volume of water is added, until the liquid is just coloured violet.  $N/10$  sodium hydroxide solution is then added, drop by drop, until an alizarin-yellow coloured precipitate is produced; 20 c.c. of pure glycerol and a few drops of phenolphthalein are next added, and the boric acid titrated with the  $N/10$  alkali.

Lunge<sup>3</sup> has shown that Wolff's indicator has no advantage over methyl orange for the analysis of borax.

The boric acid in calcium borate is determined by dissolving the sample in the least quantity of hydrochloric acid diluted with 40 c.c. of water (for 2 g. substance, 1.5 c.c. acid) with the application of heat; any carbonic acid present must be removed by heating. The solution is then titrated as above.

<sup>1</sup> *J. Soc. Chem. Ind.*, 1904, 23, 699.

<sup>2</sup> *Z. Enter. Nahr. u. Genussm.*, 1901, 4, 157.

<sup>3</sup> *Z. angew. Chem.*, 1904, 17, 203.

To determine the bases in a natural borate a sample is evaporated with hydrofluoric and sulphuric acids and the residue treated as in the method given for the examination of boric acid. For the estimation of the chlorine a portion is dissolved in nitric acid containing silver nitrate, and the filtrate from the silver chloride used for the determination of the sulphuric acid by precipitation with barium nitrate.

### 3. ALKALI FLUXES

Potassium carbonate, sodium carbonate, and sodium sulphate are employed. Potassium carbonate is used in the production of difficultly fusible potash and lead crystal glass, sodium carbonate either alone or in conjunction with potassium carbonate in the preparation of window, mirror, and lens glass, and sodium sulphate in the manufacture of window and bottle glass.

**Potassium Carbonate.**—The purity of potassium carbonate depends upon its origin and method of preparation.

It may contain sodium carbonate, chlorides, sulphates, and insoluble substances. Sodium carbonate is undesirable if the potassium carbonate is used to produce pure crystal potash glass; its presence must also, of course, be taken into account in the preparation of potash-soda glass; chlorides and sulphates cause the separation of partially fused material in the pot or tank, but with the higher temperatures now used this very seldom occurs; the insoluble constituents may introduce large quantities of alumina and of ferric oxide into the frit; also, the neglect of the amount of hygroscopic water present may introduce an error in the composition of the metal.

The examination of potassium carbonate is conducted as described on p. 543.

**Sodium Carbonate.**—This is employed partly as Leblanc and partly as ammonia soda. The Leblanc-soda often contains considerable quantities of sodium chloride and sulphate as well as substances insoluble in water; the ammonia-soda is finer and less dense, and is more frequently employed now on account of its greater purity. Although sodium carbonate is less hygroscopic than potassium carbonate, the content of water must be considered.

The examination of sodium carbonate for carbon dioxide, sodium sulphate and chloride, moisture and insoluble substances, is carried out according to the details given on pp. 454 to 460.

**Sodium Sulphate.**—Sodium sulphate has been in use for a long time as a cheap substitute for sodium carbonate in the manufacture of window and bottle glass. Since silica does not decompose sodium sulphate on heating, an addition of powdered charcoal is made in the manufacture, from 4 to 6 per cent. of the weight of the sulphate em-

ployed being added; this causes reduction to sodium sulphite, which is readily decomposed. An excess of charcoal gives rise to the formation of sodium sulphide, which dissolves in the glass and colours it yellow; since this is never quite obviated, preference is given to the dearer sodium carbonate in the manufacture of clear white bottle glass.

The sulphate is examined for the content of iron, acid sulphate, and sodium chloride; the last may cause a separation of partially fused material in the pot. The methods of analysis are given on pp. 404 to 409.

#### 4. LIME

Calcite, marble, chalk, and calcareous marl are employed, and also burnt lime subsequently slaked by the atmosphere. Unburnt lime causes much frothing of the metal during the fusion on account of the evolution of carbon dioxide, and should therefore be more or less finely powdered; this effect is avoided by using burnt lime, but then the possibility arises that the lime may contain varying quantities of water at different times and the neglect of this fact may cause faulty frits. For this reason it is occasionally necessary to estimate the quantity of calcium oxide in the sample.

The demands in regard to the purity of the lime are regulated by the kind of glass to be produced. For the preparation of green or brown bottle glass the presence of iron is in no way disadvantageous, but for colourless glass the lime must be as free as possible from iron; its presence is harmful, because it hinders the refining of the metal and produces a tendency to devitrification. Alumina is of less importance as an impurity if present in not too great quantity, because it prevents devitrification.

For the examination of lime, *cf.* p. 483.

#### 5. LEAD OXIDE

The raw materials containing lead which are of importance are red lead, litharge, lead peroxide, and calcium plumbate ( $\text{Ca}_2\text{PbO}_4$ ) which has recently been introduced. Red lead and those lead compounds which give off oxygen on heating possess an advantage over litharge because on fusion the liberated oxygen causes oxidation which serves to decolorise and purify the metal.

For the manufacture of crystal glass the above lead compounds must be free from copper and iron oxides.

An examination of the lead oxides is very essential since lead sulphate, heavy spar, alumina, sand, etc., are not uncommon impurities. To determine the content of lead a weighed quantity of the sample is dissolved by heating with dilute nitric acid and, if necessary, a very

little oxalic acid, the solution diluted with water, filtered in case there should be any insoluble residue, and after the addition of sulphuric acid evaporated until the solution begins to fume. When cold the residue is diluted with water, and the lead sulphate filtered off, washed, and weighed in the usual way. The filtrate is divided into two parts, which are examined for copper and iron respectively. Lecrenier<sup>1</sup> estimates these two metals colorimetrically by evaporating the filtrate from the lead sulphate to dryness, dissolving the residue in 1 c.c. of hydrochloric acid and a little water, and making up the solution to 500 c.c.; potassium thiocyanate is added for the colorimetric measurement in the case of iron, and ammonia in the case of copper. The insoluble residue from the nitric acid solution, if of sufficient quantity, is fused with sodium carbonate and further examined.

To determine the contained sulphates a sample is boiled with sodium carbonate solution and the solution filtered; the sulphuric acid is contained in the filtrate as sodium sulphate and the bases in the residue.

To test calcium plumbate a sample is dissolved in nitric acid with the addition of oxalic acid, the solution freed from excess of acid by evaporation, and sulphuretted hydrogen passed in to the diluted solution. The resulting precipitate is filtered, washed, and the lead and copper separated in the usual way. The sulphuretted hydrogen is then expelled from the filtrate, and the calcium, together with any traces of iron precipitated by ammonia and ammonium oxalate, filtered ignited together and weighed; the precipitate is dissolved in hydrochloric acid, and the contained iron separated by precipitation with ammonia.

## 6. OTHER OXIDES AND FLUXES

Zinc oxide, baryta, fluor-spar, and cullet are employed.

**Zinc Oxide and Baryta.**—These two oxides are now employed both more frequently and in greater quantity than formerly, especially in the manufacture of the many kinds of resistant glass which are now made, such as Jena thermometer glass and the like. Baryta is also used in place of lead oxide, since baryta glass is distinguished by its brilliant polish and high specific gravity. Zinc oxide is added to the metal as zinc white, and baryta in the form of witherite or of heavy spar. The small quantity of iron contained in these materials is estimated in the usual manner.

**Fluor-spar.**—This serves as a flux in the preparation of green glass in order to make the metal more mobile, and it is also employed to produce the cloudiness in the so-called "opal-glass"; for the latter purpose it must be as free as possible from iron.

<sup>1</sup> *Bull. Soc. Chim.*, 1904, 18, 404.

The examination of fluor-spar includes the estimation of the contained fluorine and iron. The fluorine can be determined approximately by mixing a portion of the finely powdered material with an equal quantity of pure silica in a flask, adding concentrated sulphuric acid, and determining the loss of weight due to the loss of silicon fluoride upon gently heating. A more exact estimation of the fluorine can be made by means of the Hempel fluorometer,<sup>1</sup> by which the volume of the evolved silicon fluoride is measured. Should the fluor-spar evolve carbon dioxide on treatment with acid, the Hempel-Scheffler method<sup>2</sup> must be employed, because treatment with dilute acetic acid to remove the carbonate present, does not give a correct result, as there is always a loss either of fluorine or of carbon dioxide.

For the estimation of the contained iron a portion is heated with an excess of sulphuric acid until the calcium fluoride is completely decomposed (that is, as long as hydrofluoric acid is given off), diluted with water upon cooling, and after reduction by zinc, titrated with standard permanganate solution (p. 380).

**Cullet.**—The waste produced in working up the glass metal forms a valuable addition product to the frit by means of which a considerable economy in material is made. In works where several kinds of glass are manufactured a rigid sorting of the waste is necessary. The broken glass of varying composition obtained from dealers is used as an addition in the manufacture of green or brown bottle glass, and is usually sorted according to its colour.

## 7. DECOLORISING AGENTS

The ferric oxide, sulphides, and organic substances which occur as impurities in the raw materials give the metal a more or less distinct shade of colour, even when the purest substances have been employed. To overcome this, substances are added during the fusion of the frit which effect either an oxidising action upon the colouring substance, or a colour compensation, or which produce decolorisation by both these means. The most important decolorising agents are manganese dioxide, nickel oxide, selenium, sodium selenite, arsenious acid, nitre, and compressed oxygen.

**Manganese Dioxide.**—This is the most frequently employed decolorising agent. Its action is partly due to the oxidation of the sulphides and carbon contained in the metal, and partly on account of the red-violet coloration, which is produced, and which compensates the green colour formed by ferrous oxide. The quantity employed

<sup>1</sup> Cf. Hempel's *Methods of Gas Analysis*, trans. by Dennis, p. 317.

<sup>2</sup> *Z. anorg. Chem.*, 1899, 20, 1.

is, in most cases, less than 0.05 per cent. of the metal; in some antique glass as much as 0.5 per cent. of manganese dioxide is sometimes found.

The value of pyrolusite for decolorising is proportional to its content of manganese dioxide and the smaller the quantity of ferric oxide and gangue it contains. Its examination is described under the section on "Chlorine" (p. 476).

**Nickel Oxide.**—The action of this oxide is due to the violet coloration it produces, which destroys the green coloration due to ferrous oxide. It is employed either as black oxide of nickel or as the green hydroxide, and usually in small quantities amounting to less than 0.005 per cent. of the metal.

**Selenium and Selenium Compounds.**—These agents have been quite recently employed in the decolorisation of glass, either alone or in conjunction with other decolorising agents such as pyrolusite, nickel oxide, and arsenic; reducing agents are added if necessary. The quantity of selenium employed amounts at most to 0.004 per cent. of the metal; the use of this reagent is protected by a patent.

**Arsenious Oxide and Nitre.**—These evolve oxygen and so oxidise the colouring constituents of the metal, the carbon being burnt away and the sulphides converted into sulphates which are taken up by the less fusible portions of the melt; at the same time the green coloration produced by the ferro-silicate is changed into the less noticeable pale yellow ferri-silicate.

**Compressed Oxygen** has recently been employed to decolorise the metal by passing a current of oxygen into the molten material; it serves both to oxidise and at the same time to mix the metal.

## 8. COLOURING AGENTS

The number of substances which can be employed to colour glass is extremely large. Apart from those used to produce opacity the most important colouring agents are the oxides of iron, copper, cobalt, chromium, manganese, nickel, uranium, and antimony, compounds of silver, gold, and selenium, cadmium sulphide, and various organic substances; the colouring properties of various sulphides, and of tungsten and molybdenum compounds have as yet found very little application. Many colouring agents should be examined for their content of the respective colouring substance and for their purity. Since this is conducted according to ordinary analytical methods, only those points will be emphasised which have to be particularly observed in the examination.

**Iron Compounds.**—These give a green to a wine-yellow coloration. The compounds chiefly employed are natural or manufactured ferric oxide, ferrous oxide, ferric hydroxide, ochre and ferrous carbonate;



yellow prussiate of potash and iron pyrites are less frequently used, on account of the colour produced by the contained carbon and sulphur respectively. In testing manufactured iron compounds, the presence of sulphates and chlorides as impurities should be looked for, and in the natural products the quantity of iron and the amount of gangue present should be determined.

**Manganese Compounds.**—These produce wine-red and violet to black colorations; mixed with ferric oxide, brown colorations result. Pyrolusite is generally employed; less often artificially prepared manganese dioxide or manganous carbonate. They are examined by the methods referred to under decolorising agents.

**Copper Compounds.**—With these, blue, green, and red colorations are produced. Cupric oxide and cuprous oxide are mostly used; copper sulphate is seldom employed and is not suitable. The presence of iron has a great influence on the quality of the colour, and should always be tested for.

**Cobalt Compounds.**—These produce sky-blue or dark-blue colorations according to the composition of the metal and the quantity of reagent employed. Cobalt oxide and cobaltous carbonate are most frequently employed; cobaltous phosphate or arsenate, zaffre, and smalt less frequently. A large content of nickel or of iron can seriously affect the colour.

**Chromium Compounds.**—Yellow to green colorations are produced by chromium compounds according to the composition of the glass. Chromic oxide, potassium bichromate, potassium chromate, barium lead, iron, silver, and zinc chromates are employed; chromic oxide as well as chromates produced by precipitation are not infrequently contaminated with alkali sulphates or chlorides, the presence of which must be considered in their application.

**Nickel Compounds.**—Nickel sesquioxide, nickel monoxide, and nickel hydroxide are seldom employed to colour, but more frequently to decolorise glass; they give faint reddish-brown to greenish-brown shades of colour.

**Uranium Compounds.**—Lead glass is coloured a pale- or dark-yellow by uranium compounds; with lead-free glass a yellow-green and sometimes fluorescent colour is produced. The uranium compound usually employed is uranium yellow (sodium uranate); uranic oxide or uranic-uranous oxide are less frequently used.

**Antimony Compounds.**—Antimony oxide can only be employed for glass rich in lead. Either the oxide, sulphide, or antimony-glass (a fused mixture of oxide and sulphide) is used and imparts a yellow colour. Lead-free glass is not coloured by antimony oxide, but a small quantity of metallic antimony in the frit produces increased lustre and is frequently employed for this purpose.

**Silver Compounds.**—The colouring property of silver is very great. It is employed either as oxide, carbonate, nitrate, chromate, or sulphide for the manufacture of yellow glass.

**Gold Compounds.**—Gold colours glass from pink to ruby-red according to the amount employed, and like silver possesses great colouring power; it is incorporated in the frit usually in the form of gold chloride, less frequently as purple of Cassius.

**Selenium Compounds.**—Selenium and salts of selenious acid, especially sodium and calcium selenites, have recently found extensive application for the production of pink-red glass. They are added to the frit in combination with arsenic.

**Cadmium Sulphide.**—The only compound of cadmium that colours glass is the sulphide, which produces an intense yellow.

**Organic Substances.**—Charcoal made from alder, poplar, and birch wood, graphite, and anthracite have long been employed to colour glass yellow. The reddish or gold-yellow colour which is imparted to glass by these substances is not due to these materials themselves, but to the colouring property of the sulphides, which are produced by their reducing action on the sulphates contained in the frit.

**Substances which produce Opacity.**—A great number of substances are used in glass manufacture for the production of white, more or less opaque glass. The most important of these are tin oxide, arsenic, cryolite, fluor-spar, aluminum fluoride, and sodium fluoride, in conjunction with felspar or kaolin, bone ash, guano, and fibrous asbestos. Instead of the expensive cryolite, manufactured products are now employed, which are described in commerce as artificial cryolite, cryolite substitute, milk-glass composition, albinite, opaline kryolin, etc.

*Tin oxide* is less used than *Arsenic*, which is employed rather for the production of easily fusible glass enamels than as an opacity producing material.

*Bone ash* and *Guano*, which is rich in phosphate, serve for the manufacture of milk-glass, and produce opacity on account of the phosphate of lime which they contain. Both substances are examined according to the methods given in the section on "Artificial Manures" (Vol. II.). Iron, if present, acts injuriously, and should be estimated.

*Cryolite* produces opacity on account of the contained fluorine and aluminum; the glass produced is known as opal glass. The estimation of the quantity of fluorine is carried out as given under fluor-spar; alumina, ferric oxide, and sodium oxide are determined by decomposition with sulphuric acid.

*Cryolite substitutes*, which are much recommended, consist essentially of mixtures of sodium, calcium, and aluminum fluorides, with alumina, felspar, or kaolin. When first introduced they were not only cheaper,

but also richer in fluorides than natural cryolite; recently they have been much adulterated,<sup>1</sup> so that an estimation of the contained fluorine is advisable.

*Fluor-spar* is employed in conjunction with felspar, or kaolin in the production of opal-glass, for which only iron-free varieties are permissible. The testing of this reagent has been described (p. 629).

## II. THE COMPOSITION AND TESTING OF GLASS

### THE COMPOSITION OF GLASS

It is impossible to assign a uniform formula to glass owing to the very wide variations that exist in its composition, but certain regularities can be recognised in the composition of glass of similar character, from the analytical data. The general statement propounded by Berzelius, that a glass which resists the action of water and of acids must be a double silicate containing two different bases, an alkali and the oxide of an alkaline-earth or heavy metal, has now a more limited significance owing to the recent researches of Schott, which have shown that the presence of an alkali is by no means necessary, and that it can be replaced by boric acid.

The various kinds of glass can be grouped into two main classes according to their composition:—

1. *Leadless Glass.* 2. *Lead Glass.*

*Lead-free or Leadless Glass* differs in composition according to the purpose for which it is manufactured, and can be divided into *Alkali-Lime Glass*, *Glass containing Alumina*, and *Borosilicate Glass*.

**Alkali-Lime Glass.**—This is either soda, potash, or potash-soda glass; the ratio of bases to silica, as well as that of the alkali to lime, is subject to great variation. The best lime glass, the so-called normal glass, is a tri-silicate and corresponds to the formula  $1 \text{ K}_2\text{O}(\text{Na}_2\text{O}) : 1 \text{ CaO} : 6 \text{ SiO}_2$ . Since glass of this composition is very difficult to work, the lime glass which occurs in commerce does not correspond to the above formula, but contains from 4.5 to 5  $\text{SiO}_2$  instead of 6  $\text{SiO}_2$  to the proportion of 1  $\text{CaO} : 1 \text{ K}_2\text{O}$ . Still this adjustment of the ratio of the silica is only possible within certain limits, because any considerable deviation from the normal formula produces faulty, easily decomposable glass. The properties of the glass depend also upon the nature of the alkali; potash produces colourless, difficultly fusible brilliant glass (potash-crystal) while soda glass is always of a greenish tint. Weber<sup>2</sup> is of opinion that the simultaneous presence of potash and soda is the cause of the depression phenomena in thermometers, *i.e.* of

<sup>1</sup> Cf. *Chem. Zeit.*, 1899, 23, 461.

<sup>2</sup> *Sprechsaal*, 1888, 242.

the temporary expansion of the thermometer tube in consequence of warming. An appreciable replacement of the lime by magnesia favours the tendency to devitrification, whilst the presence of a little alumina acts in the opposite direction.

**Alumina-Lime Glass.**—The composition of this glass deviates essentially from that of pure lime glass; it is employed in the production of green and brown bottles. Since the alumina replaces an acid,<sup>1</sup> the proportion of bases to silica is not 1 : 3, but mostly 1 : 1.8; on the other hand, this glass has a higher lime content, which is necessary for clear melting.

**Boro-Silicate Glass.**—Owing to the content of boric acid this glass contains either little or no alkali; it is distinguished for its small coefficient of expansion. Schott & Co. of Jena produce boro-silicate glass, in which the quantity of lime is wholly or in part replaced by other metallic oxides such as those of barium, magnesium, zinc, and antimony; this glass is used for the manufacture of thermometers, lamp glasses, chemical apparatus, etc.<sup>2</sup>

**Lead Glass.**—The composition of lead glass is similar to that of lime glass, the lime being wholly or partly replaced by lead oxide. When free from lime, it is called *Lead Crystal*, and when it contains lime, *Semi-Crystal* glass. It is softer and more easily decomposed the greater the proportion of lead present.

#### THE TESTING OF GLASS FOR RESISTANCE AGAINST THE ACTION OF THE WEATHER, WATER, AND CHEMICAL AGENTS

The weathering of glass and the greater or less extent to which it is attacked by water are, according to the researches of R. Weber and F. Förster, to be regarded as essentially similar processes; both are consequences of the decomposing action which water exerts upon the glass substance.

Weathering consists of an alteration of the surface of the glass produced by the action of atmospheric moisture which liberates alkaline substances; by the subsequent action of carbonic acid, alkali carbonates are formed which appear as an efflorescence upon the glass. The weathering is greater the more readily the glass is acted upon by water.

Concerning the influence which the composition of glass has upon its susceptibility to the action of water, O. Schott,<sup>3</sup> Stas,<sup>4</sup> Kohlrausch,<sup>5</sup>

<sup>1</sup> Cf. Frank, *Dingl. polyt. J.*, 1889, 273, 91.

<sup>2</sup> Cf. *Z. Instrumentkunde*, 1891, 331; *Verhdl. des Vereins z. Bef. d. Gewerbeleisses*, 1893, 161.

<sup>3</sup> *Z. Instrumentkunde*, 9, 81.

<sup>4</sup> *Z. anal. Chem.*, 1868, 7, 165.

<sup>5</sup> *Ber.*, 1891, 24, 3574; *Ann. Physik.*, 1891, 44, 577.

R. Weber,<sup>1</sup> E. Sauer,<sup>2</sup> P. H. Walker,<sup>3</sup> and especially Mylius and Förster<sup>4</sup> have made exhaustive studies, and have shown that the action of hot water is greater than that of cold, that at the same temperature soda glass poor in lime is less acted upon than potash glass of analogous composition, but that with increasing quantities of lime this difference gradually disappears. The proportion of lime to alkali in resistant glass should, according to R. Weber, amount to 1 CaO : 1.3 to 1.5 K<sub>2</sub>O(Na<sub>2</sub>O), and at least as much silica should be present as to represent a trisilicate which can be expressed by the formula, 2 (1 R''O : 1.3 to 1.5 R'O) : 6 SiO<sub>2</sub>. Förster and Mylius fix as the ratio for the best resistant glass the formula 1 CaO : 1.1 K<sub>2</sub>O(Na<sub>2</sub>O) : 7 SiO<sub>2</sub>. Lead glass is more resistant towards pure water than lime glass, but is easily attacked by alkalis and by acids.

The action of acids, alkalis, and other chemical agents upon glass has been examined by Weber and E. Sauer,<sup>5</sup> and very thoroughly by Förster.<sup>6</sup> As a result of these researches, the remarkable fact has been established that, in general, acids have a less marked action upon glass than water, and that concentrated acids exert a weaker effect than when dilute; the greater action of the latter is consequently ascribed to the water which they contain. The extent to which glass is attacked by water accordingly also furnishes a gauge of its resistance towards acids.

The more basic varieties of glass such as are used in the preparation of enamels, and which are only slowly attacked by boiling water, are immediately etched by dilute solutions of acids (Thomason).

Alkalis act upon glass far more strongly than water, and the degree of the effect varies but little with differences in the composition of the glass; alkali-lime glass containing alumina is the most resistant towards alkali.

The extent of the action of boiling water and of chemical reagents upon glass, as well as the connection between the power of attack and the composition, is shown in the following table (p. 637) prepared by R. Weber.

Mylius and Förster<sup>7</sup> conclude as the result of their investigations that it is not possible to judge the suitability of glass vessels for chemical purposes from their composition, because the different types of glass, such as silicate, borate, alkali-lime, alumina, and lead glass are not really comparable. This factor can only be decided by comparative tests, and F. Förster<sup>8</sup> has accordingly examined various kinds of

<sup>1</sup> *Ann. Physik.*, 1879, 6, 431; *Spechsaal*, 1891, 14; *Z. angew. Chem.*, 1891, 4, 662.

<sup>2</sup> *Ber.*, 1892, 25, 70; 1814.

<sup>3</sup> *J. Amer. Chem. Soc.*, 1905, 27, 865.

<sup>4</sup> *Ber.*, 1889, 22, 1092.

<sup>5</sup> *Ibid.*, 1892, 25, 70; 1814.

<sup>6</sup> *Ibid.*, 1893, 26, 2915; *Z. anal. Chem.*, 1894, 33, 299.

<sup>7</sup> *Z. anal. Chem.*, 1892, 31, 241.

<sup>8</sup> *Ibid.*, 1894, 33, 381.

Variety of Glass.	1	2	3	4	5	6	7	8	9	10
Action of boiling water, 5 hours	62½	31½	29½	17	13	9½	7½	7½	5	4½
Sulphuric acid, 25 per cent., 3 hours	...	43½	35	8	7	6½	5½	5	5	3
Hydrochloric acid, 12 per cent., 3 hours	85	...	21	4	2½	1½	1	1	nil	nil
Ammonia, 10 per cent., 3 hours	...	...	62	11	8½	7½	7½	6	5	5
Sodium phosphate, 2 per cent., 3 hours	...	...	31	64	40	35½	34	30	15	12½
Sodium carbonate, 2 per cent., 3 hours	283	160	130	124	50½	45	42	42	26½	25
Potassium hydroxide	23	19½	16½	10½	8½	8½	8	8	7½	7
Barium hydroxide	14	10½	8½	6	5½	5	5	5	5	4½

ANALYSES

SiO <sub>2</sub>	76.22	74.09	76.39	68.56	74.48	74.69	66.75	74.12	77.07	74.40
Al <sub>2</sub> O <sub>3</sub>	...	0.40	0.50	1.85	0.50	0.45	1.31	0.50	0.30	0.70
CaO	4.27	5.85	5.50	7.60	7.15	7.85	13.37	8.55	8.10	8.85
K <sub>2</sub> O	...	7.32	4.94	2.24	6.64	8.64	15.50	4.86	3.75	4.40
Na <sub>2</sub> O	19.51	12.34	12.67	19.75	11.23	8.37	3.07	11.97	10.78	11.65
Molecular proportions:	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00
SiO <sub>2</sub> : CaO : { $\frac{Na_2O}{K_2O}$ }	17.1:4	11.1:2.6	12.7:1.2	10:1.3	9.5:1.2	8.8:1.1:6	4.5:1.0:8	8.1:1.6	8.8:1.1:5	8.1:1.5

glass, which had been previously proved to be exceptionally good, in respect to their full behaviour towards chemical reagents.

The following tables give a summary of the results obtained. Summary I. gives the chemical composition of the various kinds of glass examined, and Summary II. the results of the investigation. The experiments show that no glass is perfectly satisfactory in its behaviour towards every kind of chemical action.

The specimens 1 to 9, which include Stas' glass (No. 4), are exceptionally resistant towards cold water; 3, 4, and 5, which are rich in lime and poor in alkali, are the most resistant to the action of hot acids.

The soda glass No. 11 containing alumina and rich in lime, is the least acted upon by sodium carbonate, ammonia, and by potassium and sodium hydroxide solutions, whilst the glass containing boric acid is very considerably altered by these reagents.

Glass No. 1 resists the action of steam best, and is therefore specially adapted for the water-gauge tubes of boilers.

The best glass at present made for chemical purposes are the "Stas,"<sup>1</sup> No. 4, and the Jena boric acid, apparatus glass; according both to F. Förster<sup>2</sup> and to F. Kohlrausch,<sup>3</sup> the latter withstands the action of water better than Stas glass and is also more resistant to sudden changes of temperature.

A variety of methods have been employed for the determination of the resistance of glass against the action of the weather, water, and chemical agents.

### Summary I.

Number of Glass.	K <sub>2</sub> O	Na <sub>2</sub> O	CaO	ZnO	MnO	Al <sub>2</sub> O <sub>3</sub> (+Fe <sub>2</sub> O <sub>3</sub> )	SiO <sub>2</sub>	B <sub>2</sub> O <sub>3</sub>	I R <sub>2</sub> O : RO : SiO <sub>2</sub>	Number of molecules of Alkali in 100 molecules.
1	...	11.0	...	...	0.05	5.0	71.95	12.0	...	10.8
2	...	9.8	7.0	5.0	0.3	3.5	74.4	...	0.84 : 1 : 6.59	10.0
3	5.8	7.6	10.4	...	...	0.3	75.9	...	0.99 : 1 : 6.81	11.2
4	6.6	6.7	9.5	...	...	0.6	76.6	...	1.05 : 1 : 7.52	11.0
5	6.2	6.4	10.0	...	0.2	0.4	76.8	...	0.95 : 1 : 7.16	10.4
6	7.0	8.3	8.1	...	...	0.3	76.3	...	1.44 : 1 : 8.80	12.7
7	11.8	4.9	7.6	...	0.1	0.5	75.1	...	1.50 : 1 : 9.24	12.8
8	4.3	10.0	7.8	...	...	0.3	77.6	...	1.48 : 1 : 9.28	12.6
9	4.6	10.1	7.7	...	...	0.4	77.2	...	1.54 : 1 : 9.36	13.0
10	...	14.0	7.0	7.0	...	2.5	67.5	2.0	1.06 : 1 : 5.41	14.0
11	0.6	14.3	11.2	...	0.4	2.9	70.6	...	1.18 : 1 : 5.88	14.6
12	14.0	1.0	5.8	...	0.1	0.2	78.9	...	1.59 : 1 : 12.7	10.4
13	1.8	12.9	11.0	...	...	1.3	73.0	...	1.16 : 1 : 6.20	13.8
15	9.7	9.0	6.8	...	Trace	0.4	74.1	...	2.04 : 1 : 10.17	15.4
16	6.7	13.7	7.2	...	0.3	3.2	68.9	...	2.27 : 1 : 8.91	18.6
17	12.7	...	...	PbO 80.0	...	...	57.3	...	1.00 : 1 : 7.10	11.0

<sup>1</sup> Manufactured at Cologne by E. Leybold.

<sup>2</sup> *Z. anal. Chem.*, 1894, 33, 396.

<sup>3</sup> *Ibid.*, 1895, 34, 592.

## Summary II.

Consecutive Number.	Approximate description of the Glass.	Alkali dissolved by water expressed in thousandths of a milligram $\text{Na}_2\text{O}$ , in:—		Ratio of alkali dissolved by hot and by cold water.	Loss of weight in milligrams at $100^\circ$ by the action of 2N solutions of alkali.		Loss in milligrams on treatment with water at $190^\circ$ for 4 hours.			
		8 days at $20^\circ$	8 hours at $80^\circ$		Sodium Hydroxide.	Sodium Carbonate.	Total loss.	Loss of Alkali.	Weight of $\text{Na}_2\text{O}$ corresponding to the dissolved alkali.	Number of molecules of $\text{SiO}_2$ dissolved by water at $100^\circ$ for each molecule of $\text{Na}_2\text{O}$ .
1	Sodium boro-silicate free from lime .	2.5	2.7	1.1	67.3	23.5	23.7	3.5	3.5	6.0
2	Zinc-lime glass containing alumina and poor in sodium	2.1	6.3	3.0	39.7	17.6	...	...	...	...
3	Glass rich in lime and poor in alkali	10.7	28.4	2.65	35.4	...	...	...	...	...
4	Similar . . .	8.9	28.2	3.17	37.5	59.5	17.2	5.6	4.6	2.65
5	Similar . . .	13.1	26.8	2.05	...	...	...	...	...	...
6	Good lime alkali glass . . .	14.0	56	4.00	39.8	76.9	...	...	...	...
7	Similar . . .	14.5	45	3.10	37.7	79.2	51.3	15.4	11.1	3.35
8	Similar . . .	14.9	50	3.40	38.5	73.0	...	...	...	...
9	Similar . . .	17.8	66	3.72	42.4	79.4	67	16.4	14.7	3.57
10	Lime-soda glass, containing zinc oxide and alumina .	16.6	65	3.91	46.5	23.0	34	6.4	6.4	4.42
11	Soda glass rich in lime and containing alumina .	27	98	3.63	31.3	40.7	?	7.3	7.3	...
12	Good potash glass poor in lime .	...	...	...	...	...	63	16.2	10.7	4.5
13	Soda glass rich in lime . . .	...	...	...	...	...	37	8.3	8.3	3.6
15	Glass rich in alkali .	32	217	6.78	...	...	...	...	...	...
16	Soda glass rich in alkali, containing alumina . .	77	654	8.50	46	45	126	61	52	1.3
17	Flint glass . .	74	350	4.73	58	51	...	...	...	...

To determine rapidly whether a glass can be described as good or bad, in regard to its resistant qualities, the hydrochloric acid test intro-



duced by R. Weber is satisfactory. The sample piece to be tested is cleansed with water and then with alcohol and placed on glass rods supported on the sides of a dish which contains fuming hydrochloric acid; the dish is covered by a bell-jar, and the sample subjected to the action of the vapours for twenty-four hours. When the action is complete the condensed acid vapour is allowed to evaporate in a dust-free place. With poor qualities of glass a considerable incrustation is formed; with better qualities there is less incrustation, and only a slight film with good glass which almost entirely disappears with the best varieties.

For the examination of imperfectly compounded glass R. Kissling<sup>1</sup> places the glass for several days in contact with standardised, weak alcoholic sodium hydroxide solution. A separation of sodium silicate soon occurs with bad glass; the alkalinity of the solution decreases, of course, in proportion to its effect, and the extent of the action is determined by titrating back the unchanged alkali.

A qualitative test suitable for testing glass vessels for their resistance against the action of water is given by Mylius.<sup>2</sup> The glass vessels are first carefully rinsed out successively with water, alcohol, and ether, and then treated, before the ether has evaporated, with a solution of eosine made by saturating ordinary ether with water, and dissolving 0.1 g. of iodo-eosine in 100 c.c. of the mixture. The solution is allowed to act for twenty-four hours, then poured off, and the vessel rinsed with ether. The surface of the glass is covered with a more or less intensely coloured layer according to the ease with which it is attacked.

The quantitative examination of the resistance of a definite variety of glass is most simply carried out by the method employed by R. Weber and E. Sauer.<sup>3</sup> The vessels selected for comparison should be such that their capacity or internal superficial area can be accurately measured or calculated. They are first cleansed by repeated rinsing with distilled water and alcohol, carefully dried, and weighed; then they are filled with distilled water so that in each vessel as nearly as possible the same amount of surface is wetted, and the height of the liquid recorded. The vessels are then heated upon a sand-bath or asbestos card to boiling, care being taken that all the vessels tested are heated as uniformly as possible, and that the evaporated liquid is, from time to time, replaced. After from three to five hours the boiling is stopped, the vessels emptied, dried, and weighed; the loss of weight is calculated per 100 sq. cm. of surface. To test the action at temperatures other than that of boiling water the vessels are heated in a paraffin or air bath which is carefully kept at the required temperature. Since distilled water stored in glass vessels, and therefore containing alkali, is used in this method, no absolutely exact values are obtained, but the compara-

<sup>1</sup> *Z. anal. Chem.*, 1898, 37, 321; *Chem. Zeit.*, 1895, 19, 1682.

<sup>2</sup> *Ber.*, 1889, 22, 310; *Z. anal. Chem.*, 1891, 30, 247.

<sup>3</sup> *Ber.*, 1892, 25, 70.

tive results are of value, and the method has the advantage of being quick and easily carried out. The resistance to acids and to alkalis can be determined in the same way.

Förster and Mylius<sup>1</sup> determine the action of water by first treating the vessels for three days with perfectly pure so-called "neutral" water at 20°, for the purpose of removing any accidentally disintegrated material; this solution is then poured off, the vessel treated afresh for three days with neutral water at 20°, and the dissolved alkali estimated colorimetrically by means of  $N/1000$  iodo-eosine solution. The quantity of alkali found furnishes a measure of the action. The method yields very exact results, but the preparation of the neutral water and of the iodo-eosine solution offers so many difficulties that the application of the method is very limited.

The method devised by E. Pfeiffer and F. Kohlrausch<sup>2</sup> to determine the extent to which glass is attacked by water from the alteration of the electrical conductivity, due to the substances dissolved from the glass by the water, is too intricate for technical work.

### III. THE ANALYSIS OF GLASS

The chief constituents of colourless glass and of green bottle glass are silica, boric acid, alumina, ferric oxide, calcium, magnesium, potassium, sodium, manganese, and lead oxides; barium, zinc, and antimony oxides occur less frequently. Coloured and opaque glass may contain in addition phosphoric acid, fluorine, selenium, the oxides of tin, copper, cadmium, arsenic, cobalt, nickel, chromium, uranium, and sulphides.

It is only in exceptional cases that it is possible to know in advance what constituents are contained in the glass under examination. Since the method adopted for the quantitative analysis of the glass depends upon the presence or absence of individual constituents, a previous qualitative examination is in most cases necessary.

#### QUALITATIVE EXAMINATION

1. *Examination for all constituents except Silica, Boric acid, and Fluorine.* A somewhat large quantity of the glass, about 5 g., is decomposed with pure hydrofluoric acid and some sulphuric acid in the manner described below. The residue obtained on evaporation is then heated with hydrochloric acid and water; in the absence of barium or of large quantities of lead and zinc oxides a clear solution results which is tested according to the usual method of analysis.

<sup>1</sup> *Z. anal. Chem.*, 1892, **31**, 241.

<sup>2</sup> *Ann. Physik.*, 1891, **44**, 239, 257; *Ber.*, 1891, **24**, 3560.

If a residue remains, it may consist of barium and lead sulphates or of meta-stannic acid, and if coloured violet or red it may contain also gold or selenium. It is filtered off and boiled first with a concentrated solution of ammonium acetate which dissolves the lead sulphate; if a residue remains, it is filtered off, boiled with sodium carbonate solution, filtered, and the residue, after washing, treated with hydrochloric acid, which dissolves any barium carbonate formed. The solutions are tested for lead and barium respectively. The residue which sometimes remains is treated with aqua regia if its colour suggests the presence of gold, and after filtering, fused with sodium carbonate and sulphur to test for tin; the fused mass is dissolved in water and hydrochloric acid added, when a precipitate of stannic sulphide is formed if tin is present.

To identify selenium, about 5 g. are heated in a platinum dish with hydrofluoric acid upon a water-bath until completely decomposed, and the hydrofluoric acid evaporated. The resulting red-coloured residue is moistened with concentrated nitric acid, evaporated to dryness, the mass treated with a little water, the solution filtered into a small porcelain dish and tested for selenium with hydrochloric acid and stannous chloride or with hydrochloric acid and sulphurous acid. A brick-red coloration or a distinct precipitate of selenium is immediately formed if the latter is present.

If the glass has to be quickly tested for the presence of lead, a sample is decomposed with hydrofluoric and nitric acids, evaporated to dryness, dissolved in a little nitric acid and largely diluted with water, filtering if necessary; sulphuretted hydrogen is then passed into the diluted solution. Another quick method, but which requires practice, is to heat a small piece of the glass for from one to two minutes in the blowpipe oxidising flame; lead glass forms a more or less blackened iridescent surface.

2. *Silica, Boric acid, and Fluorine.* An examination for silica is only necessary in exceptional cases, and is then carried out in the usual way.

For the detection of boric acid, the method worked out and tested by E. Adam is to be strongly recommended. About 0.5 to 1 g. of the finely powdered glass is added to hydrofluoric acid in a platinum crucible, stirred with a platinum wire and the whole evaporated to dryness on a water-bath. Upon cooling, a few drops of concentrated sulphuric acid are added, the whole well stirred, the crucible covered with the lid so as to leave a narrow opening, placed upon a triangle and carefully heated by means of a Bunsen burner provided with a rose-piece, while at the same time a non-luminous Bunsen or spirit lamp flame is so held over the crucible that the vapours escaping through the opening must pass this flame. If boric acid is present a more or less vivid green coloration

tion of the flame takes place after the heating has been continued for a short time. The reaction is so sensitive that even 0.1 per cent. of boron trioxide can be distinctly identified. With a little practice this test can be made during the decomposition of the glass for qualitative analysis.

For the identification of very small quantities of boric acid in glass (up to 0.01 per cent.), Rosenblatt's method as modified by E. Adam can be used. About 1 g. of finely powdered glass is decomposed in a platinum crucible with hydrofluoric acid by evaporation upon a water-bath, the residue stirred with concentrated sulphuric acid to a thick paste and placed in a small test-tube fitted with a double-bored cork furnished with two tubes; one of these is a glass tube which reaches nearly to the bottom of the test-tube, and the second a porcelain tube similar to that used with a Rose's crucible and ending just beneath the cork. A current of hydrogen is passed through the apparatus and ignited at the end of the porcelain tube and the contents of the test-tube carefully heated; considerable frothing occurs at first, and hydrogen fluoride is evolved which colours the hydrogen flame a pale blue; the flame should be from 2 to 3 cm. long. After from one to two minutes, when the frothing has ceased, the tube is more strongly heated, and after a time a distinct green coloration of the hydrogen flame is observed which is even apparent when the glass contains only 0.01 per cent. of boron trioxide; with greater quantities the coloration persists for a considerable time.

To identify fluorine, a sample of the glass is fused with four times its weight of sodium-potassium carbonate, the mass treated with water, the extract filtered, concentrated by evaporation, and allowed to cool; the solution is then placed in a platinum dish, hydrochloric acid added until the liquid reacts weakly acid, and allowed to stand until the carbon dioxide has escaped. An excess of ammonia is then added, the solution filtered into a flask, calcium chloride solution added to the liquid whilst still hot, and the closed flask allowed to stand. If a precipitate is deposited after a time, it is collected upon a filter, dried, and after admixture with finely divided silica, placed in a small glass flask which is closed with a cork fitted with an inlet and outlet tube. A slow current of dry air is passed through the inlet tube which reaches to the bottom of the flask; the air escapes through the outlet tube which ends close beneath the cork, and which is attached to a small U-shaped tube in which there is a bulb containing a few drops of water. The flask is then heated to about  $160^{\circ}$ , when silicon fluoride is evolved which escapes with the air and is decomposed by the water with the separation of flakes of silica, which can be easily recognised.

## . QUANTITATIVE ANALYSIS

**Preparation of the Substance for Analysis.**—Glass need not be powdered especially fine for complete decomposition on fusion to be effected, as is often erroneously stated to be necessary. The simplest plan is to strongly heat and then suddenly chill the sample, crush it in a smooth porcelain mortar, then sift it through fine gauze, and finally grind it in an agate mortar until no coarse particles remain.

In cases where an exact determination of iron is of minor importance, the grinding can be done in a hard-steel diamond mortar. For this purpose one-third of the cylinder is filled with the glass previously chilled as above or broken into small pieces with a hammer; the pestle is then inserted and struck a good blow, the contents of the mortar stirred, again struck with the pestle, and passed through a correspondingly fine sieve. The residue is similarly treated, and the sifted powder ground in an agate mortar to the required degree of fineness. It is impossible by this method to avoid the powdered glass being contaminated with a small quantity of iron, which cannot be removed either by mechanical or by chemical means without decomposing the glass.

**Decomposition.**—Two decompositions generally suffice for the analysis. Fusion with sodium carbonate for the estimation of silica and the other constituents with the exception of the alkalis and decomposition with either hydrofluoric acid or with calcium carbonate and ammonium chloride, for the estimation of the latter.

Where the qualitative analysis has shown that certain constituents are present in very small quantities, it is quicker and more accurate if the fusion with sodium carbonate is used only for the estimation of silica, and a third larger quantity (about 5 g.) decomposed with hydrofluoric acid for the estimation of the remaining constituents, in addition to the decomposition for the estimation of the alkalis.

**1. Leadless Alkali-lime and Alumina-lime Glass.**—At least two decompositions are necessary for the analysis.

*Fusion with Sodium Carbonate.* From 1 to 5 g. of the powdered glass are placed in a capacious platinum crucible, about four times the quantity of pure, dry sodium carbonate gradually added, and the whole well mixed with a stout platinum wire or with a glass rod with fused ends. The particles adhering to the wire or to the glass rod are brushed into the crucible, the latter well covered with the lid, placed on either a platinum or porcelain triangle, and at first carefully heated, taking care not to let the crucible get red-hot. After a short time the heat is increased so that portions of the side of the crucible are successively raised to a dull red heat, the heating of the bottom of the crucible being avoided. When the outer portions of the contents of the crucible are fused the

bottom of the crucible is gradually heated until the whole is melted, finally heating for a few minutes over the blowpipe flame. The lid of the crucible is then removed and a stout piece of platinum wire of convenient length and bent at the end into a loop inserted, and the contents allowed to cool. When the mass has so far cooled as to grip the loop of platinum wire, the crucible is again heated on the blowpipe, and the fused mass withdrawn from the crucible by gently pulling. The crucible and lid after cooling are placed in a large beaker with 100 c.c. of hot water, and after a short time, when the residue of the melt has become soft, both are removed and any adhering matter washed or rubbed off with hot water; particles which adhere stubbornly are dissolved off by means of a few drops of hydrochloric acid, and added to the main solution. The fused mass adhering to the platinum wire is then suspended in the liquid until it has become soft, the wire withdrawn and cleansed similarly to the crucible and lid, the beaker covered with a clock-glass, and the solution gradually and carefully acidified with hydrochloric acid. It is then heated until no more carbon dioxide is evolved, and finally evaporated to dryness in a platinum basin upon the water-bath for the separation of the silica.

If a large platinum basin of at least 200 c.c. capacity is available, and the colour of the melt indicates that no large quantity of manganese is present, both the solution and the decomposition by hydrochloric acid can be conveniently effected in the basin itself; the acid should be added by means of a pipette and the basin kept covered by a clock-glass as a protection against spitting and frothing over. This method is not applicable in presence of much manganese, since it is contained in the melt in the form of sodium manganate; reduction would accordingly take place on the addition of hydrochloric acid with the evolution of chlorine which would attack the platinum.

When the contents of the basin have been so far evaporated as to become pasty, they are stirred frequently with a platinum wire or glass rod to hasten the evaporation, and also to prevent the formation of coarse lumps which dry with difficulty. The evaporation is continued until no more fumes of hydrochloric acid are given off; the residue is then heated for some hours in an air-bath from  $110^{\circ}$  to  $120^{\circ}$ , so as to dry it thoroughly and to effect as complete a separation of the silica as possible. When cold, the mass is moistened uniformly with hydrochloric acid of sp. gr. 1.12, covered with a platinum lid or clock-glass, and warmed on the water-bath for half an hour; about 20 c.c. of hydrochloric acid and from 100 to 150 c.c. of water are then added, the whole well stirred, heated on the water-bath for a short time, and the separated silica filtered off. This is best carried out by first pouring the clear liquid only through the filter, and washing the precipitated silica by decantation, with hydrochloric acid and hot water, in the basin

before finally transferring it to the filter, where it is washed with hot water until the washings cease to give a turbidity with silver nitrate solution.

The observations of Linde,<sup>1</sup> Gilbert,<sup>2</sup> and Craig<sup>3</sup> have shown that it is not possible to completely separate the silica with only one evaporation, and more recently both Adam and Hillebrand<sup>4</sup> have proved that even repeated evaporation with hydrochloric acid and subsequent drying is not satisfactory, unless the separated silica is filtered off after each evaporation. It is accordingly essential to again evaporate the filtrate from the silica, obtained as above, in a similar manner. In order to save time, the evaporation of the washings can be dispensed with; they are therefore collected apart from the original filtrate, and may be used to dissolve the residue obtained by the second evaporation.

The residue of silica thus obtained is collected upon a specially small filter, washed, and thoroughly dried; the main portion of the precipitate is also dried thoroughly. The small quantity of silica, together with the filter paper, is then placed in a weighed platinum crucible, and at first very carefully heated, then more strongly, until the filter ash is completely burnt; the chief portion of the silica, together with the filter, is then added, in like manner carefully heated, and finally ignited over the blowpipe until the weight is constant. The crucible is allowed to cool in a desiccator, and weighed as soon as possible, since the silica is very hygroscopic. In exact analyses, the purity of the weighed silica is checked by evaporating with pure hydrofluoric acid; should the residue be significant it must be dissolved in hydrochloric acid, or fused with acid potassium sulphate and examined.

The filtrate from the silica is first warmed with a few drops of concentrated nitric acid, in order to oxidise the ferrous iron, and in absence of weighable quantities of manganese salts, ammonium chloride, and ammonia free from carbon dioxide, are added in slight excess, and the solution boiled for a short time, whereby ferric oxide and alumina are precipitated. The presence of any considerable quantity of manganese is shown by the dark green colour of the melt and of the aqueous solution. The precipitate is filtered off, washed, and whilst still moist, placed in a weighed platinum crucible, in which it is ignited and weighed. The calcium is precipitated in the filtrate by means of ammonia and ammonium oxalate, the solution boiled for a short time, the precipitated calcium oxalate allowed to stand for six to eight hours, filtered, and weighed as calcium oxide. For the separation of calcium and magnesium, *cf.* p. 405.

Finally the magnesium is separated in the filtrate from the calcium

<sup>1</sup> *Chem. News*, 1889, 60, 14, 33, and 41.

<sup>2</sup> *Technol. Quarterly*, 3, 61; *Z. anal. Chem.*, 1889, 29, 688.

<sup>3</sup> *Chem. News*, 1889, 60, 227.

<sup>4</sup> *J. Amer. Chem. Soc.*, 1902, 24, 362.

by means of ammonia and sodium phosphate, and after standing twenty-four hours, the resulting precipitate of magnesium ammonium phosphate, filtered, washed with dilute ammonia, dried, ignited until the weight is constant; and weighed as magnesium pyrophosphate.

Should the quantity of ferric oxide be so great, as is the case with green or brown bottle glass, that its separation from alumina is necessary, the iron-alumina precipitate is fused with acid potassium sulphate, the melt dissolved in water, and the iron determined with permanganate after reduction with zinc (*cf.* p. 380). The alumina is taken by difference.

If small quantities of antimony oxide, ferric oxide, or of manganous oxide are to be determined, they, or the total bases, with the exception of the alkalis, are estimated in a separate portion of about 5 g. by decomposition with hydrofluoric and sulphuric acids. If only ferric oxide has to be determined, the resulting sulphuric acid solution is reduced by zinc, and titrated with permanganate solution. Should the other oxides have to be estimated, then the excess of sulphuric acid employed in the decomposition is removed by evaporation, the residue dissolved in dilute hydrochloric acid, and the antimony precipitated by sulphuretted hydrogen. The excess of the latter is then removed from the filtrate by boiling, the solution oxidised with nitric acid, neutralised with sodium carbonate, and the alumina and ferric oxide precipitated by means of sodium acetate. The manganese is then separated in the filtrate by the addition of bromine, and the calcium and magnesium estimated as usual.

The separation of manganous oxide from alumina and ferric oxide can also be effected by adding a relatively large quantity of ammonium chloride solution to the solution oxidised by nitric acid, and precipitating the alumina and ferric oxide with ammonia, dissolving the filtered precipitate in hydrochloric acid, and reprecipitating in a similar manner; the manganese in the united and concentrated filtrates is then separated from the calcium and magnesium by means of ammonium sulphide.

*Decomposition with Hydrofluoric Acid.* From 1 to 2 g. of the powdered sample moistened with a little water are placed in a large platinum basin, perfectly pure hydrofluoric acid carefully added, and the whole well mixed by a thick, bent platinum wire; a considerable evolution of heat occurs. The basin is covered with a shallow, dome-shaped platinum cover, heated for a few hours on the water-bath, or allowed to stand overnight, and after the decomposition is complete, the contents evaporated to dryness on the water-bath. The resulting fluorides are stirred to a thin paste with a little water and dilute sulphuric acid (1 : 1), evaporated first on the water-bath and then on an asbestos card over a rose-Bunsen burner; the temperature is gradually raised so as to



drive off the sulphuric acid. The dish should be kept covered with a platinum cover until dense fumes of sulphuric acid escape, in order to prevent loss by spiriting, which may occur during the decomposition of the fluorides with sulphuric acid, in consequence of the escaping fumes of hydrofluoric acid and of silicon fluoride carrying away particles of the substance. The heating of the dish is then discontinued, and the cover heated by the flame from above until no more fumes are evolved, when it is taken off and the contents of the dish strongly heated, so that the bottom of the basin is brought to a dull red heat. After cooling, the sulphates are moistened with concentrated hydrochloric acid, hot water added, the dish again covered with the lid and heated until complete solution is effected. Hot barium chloride solution is then added to the boiling, dilute solution so long as precipitation occurs, in order to remove the sulphuric acid, and, without previous filtering, ammonia and carbonate of ammonium are added in slight excess for the removal of the ferric oxide, alumina, calcium, and the excess of barium chloride. When the resulting precipitate has settled a few drops of ammonia and of ammonium carbonate are added to ensure complete precipitation, the precipitate filtered off and washed, the filtrate evaporated to dryness on the water-bath, and the residue carefully heated without allowing the basin to become red hot, so as to remove ammonium salts. The residue is then dissolved in water, the solution boiled with a little pure calcium hydroxide to remove any small quantity of magnesium present, and the calcium and any small residue of barium separated from the filtered solution by the addition of ammonia, ammonium carbonate, and a trace of ammonium oxalate. The filtrate is evaporated to dryness in a weighed platinum basin, the residual chlorides carefully heated to ensure the complete removal of ammonium salts, then gently ignited and weighed, after allowing to cool in the desiccator.

For the separation of potassium from sodium the chlorides are dissolved in a little water and the potassium precipitated as potassium platinichloride in the usual way, by the addition of platinic chloride (*cf.* p. 520). The filtered precipitate of potassium platinichloride can either be reduced to platinum by ignition in a current of hydrogen and weighed as such, or it can be dried upon the filter paper, washed with hot water into a weighed platinum basin, evaporated to dryness, dried in an air-bath at  $130^{\circ}$ , and weighed. The weight of potassium chloride thus found is deducted from the weight of the total chlorides, and the weight of sodium chloride present obtained by difference.

A somewhat less accurate but very rapid method for the estimation of potassium and sodium is to add to the aqueous solution of the alkali chlorides a little nitric acid and 5 c.c. of a saturated solution of iron alum, and to determine the total chlorine volumetrically by Volhard's method (p. 123) with silver nitrate and ammonium thiocyanate solutions ;

the proportions of potassium chloride and of sodium chloride are then calculated indirectly.

M. Müller<sup>1</sup> and Appert and Henrivaux<sup>2</sup> give the following rapid method for the estimation of the alkalis in glass. One gram of finely powdered glass is evaporated twice with eight times its weight of ammonium fluoride, and then heated to a dull red heat; when cold a few drops of concentrated sulphuric acid are added, the product carefully evaporated and ignited to decompose the acid salts. The sulphates are taken up with water, 2 g. of pure, powdered barium hydroxide added without filtering, and the whole allowed to settle for half an hour, when the precipitate of barium sulphate, aluminum hydroxide, and ferric hydroxide is filtered off. The excess of barium, together with the calcium and magnesium, are precipitated in the filtrate by passing in carbon dioxide, then boiling for ten minutes, and filtering; the filtered solution is acidified with hydrochloric acid, evaporated to dryness, the residue dissolved in water, ammonium carbonate added to remove the last traces of barium, calcium, and magnesium, and the filtrate, which contains the alkali chlorides, evaporated, gently ignited, and weighed.

*Decomposition with Calcium Carbonate and Ammonium Chloride.*

This method, which is due to J. Lawrence Smith,<sup>3</sup> can also be used for the estimation of the alkalis in glass, and is preferable to the decomposition with hydrofluoric acid if boric acid or magnesia are present, as these substances remain behind with the insoluble salts after the fused mass is lixiviated with water (W. Thomason).

From 0.5 to 1 g. of the powdered sample is heated in a platinum crucible with a mixture of 1 g. of sublimed ammonium chloride and 8 g. of pure calcium carbonate, at first quite gently until no more ammonia is evolved, and then to a dull red heat for fifty to sixty minutes. The fused mass, after cooling, is lixiviated with water in a platinum dish, the solution filtered, the residue thoroughly washed, and the filtrate, which contains the alkali chlorides, calcium chloride, and ammonium salts, treated with ammonia and ammonium carbonate. The precipitated calcium carbonate is dissolved and reprecipitated so as to completely remove any small quantity of alkali that may be retained, and the united filtrates evaporated to dryness. The ammonium salts are then removed by gentle ignition, the residue dissolved in a little water, and the last traces of calcium precipitated by means of ammonia and ammonium oxalate. The filtrate from the calcium precipitate is again evaporated to dryness, gently ignited, the residue carefully moistened with hydrochloric acid to convert any carbonate present into chloride, the evaporation and ignition repeated, and the resulting chlorides

<sup>1</sup> Post, *Chemisch technische Analyse*, 1890, vol. ii., p. 100.

<sup>2</sup> *Verre et Verrerie*, 1894, 65.

<sup>3</sup> *Amer. J. Soc.*, 1871, 50, 269; cf. Treadwell, *Analytical Chemistry*, vol. ii., p. 394.

weighed. The separation of the sodium and potassium can then be effected in the residue as described above.

Appert and Henrivaux, Knapp<sup>1</sup> and E. Adam, have shown that sodium sulphate is present in many kinds of glass; especially when sulphate is employed as a flux in their manufacture. To estimate it, from 1 to 2 g. of glass are fused with sodium carbonate free from sulphate, and after the removal of the silica the sulphuric acid determined in the filtrate by precipitation with barium chloride.

**2. Lead Glass.**—The method of analysis of lead glass depends upon whether it is semi-crystal glass which contains calcium, or flint glass which is free from calcium.

*Semi-Crystal Glass.* Two decompositions are necessary for the analysis of lead glass containing calcium; one with hydrofluoric and sulphuric acids for the estimation of the alkalis, and the other with sodium carbonate for the estimation of the other bases and silica.

The hydrofluoric acid decomposition is carried out as previously described. The residue, after the removal of the sulphuric acid, is heated with hydrochloric acid and water, the undissolved portion of the lead sulphate filtered off, and the filtrate proceeded with exactly as with lead-free glass. To prove whether the decomposition with hydrofluoric and sulphuric acids has been complete, it is advisable to warm the residue of lead sulphate with ammonium acetate solution, when a clear solution should result.

The fusion with sodium carbonate does not differ from the method adopted with lead-free glass; there is no danger of the platinum crucible being attacked even with glass very rich in lead unless reduction, which can only be caused by great carelessness, takes place during the fusion. The addition of potassium nitrate so often recommended is, according to the experience of E. Adam, quite superfluous; it causes a troublesome frothing of the crucible contents during the fusion and makes the decomposition of the melt with hydrochloric acid in platinum vessels impossible. The heating of the mixture with the blowpipe flame is in most cases dispensed with, since lead glass fuses more readily and is therefore more easily decomposed than leadless glass. The fused mass after it has been softened with water is decomposed either with nitric acid or with hydrochloric acid and the silica separated by evaporation. The use of nitric acid is advantageous in so far as it avoids the formation of difficultly soluble lead chloride, and the lead sulphide precipitated by sulphuretted hydrogen in the filtrate can be directly ignited in a current of hydrogen and weighed, but if it is used in too large a quantity it prevents the complete precipitation of the lead sulphide. From the latter consideration E. Adam regards it as preferable to use hydrochloric acid, due precaution being taken for the complete separa-

<sup>1</sup> *Sprechsaal*, 1895, 466.

tion of the silica from the precipitated, difficultly soluble lead chloride by filtering the solution as hot as possible and washing the silica several times with hot water, both by decantation and on the filter. By this means it is easy to completely remove the lead chloride without using large quantities of liquid. It is necessary to evaporate and separate the silica twice, as in the case of lead-free glass (*cf.* p. 646).

The lead is precipitated as lead sulphide by sulphuretted hydrogen in the filtrate from the silica, which must not contain too much free acid; should any lead chloride in the form of needles be deposited on the bottom of the beaker before the treatment with sulphuretted hydrogen, the liquid is warmed and stirred until the lead chloride is dissolved, cooled quickly to the ordinary temperature by placing in cold water, and sulphuretted hydrogen passed in before a fresh separation of the chloride can occur.

The lead sulphide is filtered off and well washed, and if it has been precipitated from nitric acid solution it can, after previous ignition in a current of hydrogen, be directly weighed as such; it is preferable, however, to dissolve it in nitric acid and convert it into lead sulphate. This latter method is adopted with the precipitate obtained in hydrochloric acid solution, and which contains lead chloride. For this purpose the moist lead sulphide is washed from the filter paper into a beaker, nitric acid of sp. gr. 1.2 added, and gently heated until the lead sulphide is dissolved and only particles of sulphur float in the solution; it is then filtered into a porcelain basin, sulphuric acid added to the filtrate, evaporated until the sulphuric acid begins to give off fumes, the residue diluted with water and the lead sulphate filtered off, washed, and dried. The filter paper on which the original precipitate of lead sulphide is collected and to which some still adheres, is first ignited in a porcelain crucible, and the residue evaporated with nitric acid and a few drops of sulphuric acid; the lead sulphate is then added, ignited, and the whole weighed.

The separation and estimation of the remaining bases in the filtrate from the lead sulphide is effected by heating the solution to remove the dissolved sulphuretted hydrogen and then proceeding according to the method given above for lead-free glass.

*Flint Glass.* The analysis of flint glass can be conducted similarly to that of semi-crystal glass, but the following method is quicker. A fusion with sodium carbonate for the estimation of silica is necessary, and a decomposition with hydrofluoric acid and sulphuric acid for the estimation of the alkalis; in addition a third portion is decomposed with hydrofluoric acid and nitric acid for the estimation of lead oxide, alumina, ferric oxide, manganese oxide, and of the somewhat small quantities of calcium and magnesium which are present. The two first decompositions are carried out as described for semi-crystal glass. For

the third decomposition, hydrofluoric acid is added to from 1 to 2 g. of the powdered sample in a platinum basin, and after digesting for some time evaporated to dryness on the water-bath; concentrated nitric acid is then poured on the residue, the whole again evaporated to dryness and taken up with nitric acid and hot water, when a clear solution should result. Excess of sulphuric acid is added to separate the lead, the solution evaporated to half its volume, diluted with water, the lead sulphate filtered off, washed first with water containing sulphuric acid and then with alcohol, ignited, and weighed. The remaining bases with the exception of the alkalis are estimated in the usual way in the filtrate, which is, of course, kept apart from the alcohol washings. With experience, the use of nitric acid in the decomposition can be avoided, a greater proportion of sulphuric acid being employed in its place; if this is done the sulphuric acid must not be entirely driven off, and special care must be taken to see that the decomposition is complete.

The separate decomposition for the estimation of the alkalis can be omitted if no magnesium is contained in the glass, because they can then be determined with the remaining bases; in this case the excess of sulphuric acid must be removed by evaporation after the separation of the lead, before proceeding to estimate the remaining constituents.

**3. Glass containing Boric Acid.**—The boric acid present in glass is generally determined by difference, on account of the somewhat lengthy character of the direct methods of estimation. Hönig and Spitz<sup>1</sup> estimate the boric acid in silicates by the following volumetric method. The finely powdered substance is decomposed by fusion with potassium-sodium carbonate, the melt extracted with water, an ammonium salt added in at least equivalent quantity to the alkali carbonate employed, and the solution boiled for some time; an ammoniacal solution of zinc oxide is then added to precipitate the last traces of silica, the solution heated until all the ammonia is removed, filtered, and the insoluble residue washed. The filtrate is evaporated to as small a volume as possible, rinsed into a flask, and after the addition of methyl orange, boiled for ten to fifteen minutes with a slight excess of  $N/2$  hydrochloric acid, using a reflux condenser. When cold, the condenser tube is rinsed with water into the flask, methyl orange again added, and the excess of hydrochloric acid neutralised with alkali. The boric acid is then estimated in the neutralised solution as described on p. 624. For the gravimetric estimation of boric acid a weighed sample of glass is fused with four times its weight of pure potassium carbonate, the mass dissolved by hot water (if the solution is coloured green by potassium manganate, alcohol is added), filtered, and the residue washed with hot water. The filtrate, which contains silicate, borate, and

<sup>1</sup> *Z. anal. Chem.*, 1903, 42, 100.

carbonate of potassium as well as potassium aluminate, is nearly neutralised by hydrochloric acid, the silica and alumina separated by ammonia and ammoniacal zinc oxide, according to the method given below for glass containing fluorine, and the boric acid in the filtrate saturated with hydrofluoric acid and estimated as potassium borofluoride.

An alternative gravimetric method is to evaporate the aqueous extract from the fusion with sodium carbonate to a small volume, acidify it with acetic acid, and determine the contained boric acid by the Rosenbladt-Gooch method,<sup>1</sup> in which it is liberated as trimethyl borate by heating with methyl alcohol and acetic acid; the trimethyl borate is then decomposed by passing it over a weighed quantity of calcium oxide in presence of water, and the increase of weight, which is due to the liberated boric acid, determined.

In the analysis of glass containing boric acid it is advantageous to make three distinct decompositions, since its presence complicates the separation of many metallic oxides. A fusion with sodium carbonate is used for the estimation of silica and of the metals precipitated by sulphuretted hydrogen; a decomposition with hydrofluoric and sulphuric acids or with calcium carbonate and ammonium chloride, for the determination of the alkalis, and the third decomposition with the same acids for the estimation of the remaining oxides, since the boric acid is liberated as boron fluoride in the reaction. After the fusion with sodium carbonate, it is first necessary to remove the boric acid, which can be completely effected by the method of Jannasch,<sup>2</sup> in which the dry residue in the separation of the silica is evaporated three or four times with methyl alcohol previously saturated with hydrochloric acid gas. A separate decomposition for the estimation of the alkalis is unnecessary in the absence of magnesium, as these can then be determined in the hydrofluoric acid decomposition solution along with the other oxides.

**4. Glass containing Fluorine.**—The estimation of the alkalis is carried out as usual by decomposition with hydrofluoric and sulphuric acids. The determination of the other bases, of fluorine and of silica, is complicated by the fact that a volatilisation of silicon fluoride would occur in the evaporation with hydrochloric acid for the separation of the silica. The following method of analysis is therefore adopted.<sup>3</sup>

A sample of the finely powdered glass is fused for a long time with potassium carbonate; if the glass is rich in fluorine, two and a half times its weight, accurately weighed, of pure ignited silica is also added. The

<sup>1</sup> *Z. anal. Chem.*, 1887, 26, 18, 364; Treadwell, *Analytical Chemistry*, vol. ii., p. 337; cf. also, Manning and Lang, *J. Soc. Chem. Ind.*, 1906, 25, 397.

<sup>2</sup> *Z. anorg. Chem.*, 1896, 12, 208; *Z. anal. Chem.*, 1897, 36, 283.

<sup>3</sup> Cf. Fresenius, *Quantitative Analysis*, 7th edition, vol. i., p. 496.

melt is boiled with water in a platinum vessel, filtered from the residue, the silica and alumina separated from the solution by boiling for some time with ammonium carbonate, filtered off, and the last traces of silica removed from the filtrate by means of ammoniacal zinc oxide; this portion of the silica is filtered separately. For the estimation of the fluorine, hydrochloric acid is added to the solution, which contains all the fluorine as potassium fluoride together with potassium carbonate, in sufficient quantity to leave one-third of the potassium carbonate undecomposed; calcium chloride solution is then added, when a precipitate consisting of calcium carbonate and calcium fluoride is produced, which is filtered, washed, gently ignited, treated with dilute acetic acid to remove the calcium carbonate, the mixture evaporated to dryness, the residue treated with water, filtered, and after washing, dried, ignited, and weighed. The quantity of fluorine present is obtained from the weight of calcium fluoride found.

For the estimation of the silica and the metallic oxides, first the precipitate obtained with the ammoniacal zinc oxide is dissolved in nitric acid, evaporated to dryness, and the silica separated from the residue, washed, ignited, and weighed. The residue left from the original extraction of the melt, together with the precipitate obtained by ammonium carbonate (after drying and removal from the filter paper, which is incinerated and gently ignited), are then dissolved together with the ash in hydrochloric acid, the silica separated from the solution and the weight added to that previously determined; the metallic oxides present are then estimated in the filtrate. A more rapid method for the determination of the metallic oxides is to decompose a portion of the glass with hydrofluoric and sulphuric acids and to estimate the bases in the resulting solution.

**5. Glass containing Phosphoric Acid.**—The presence of phosphoric acid in a glass such as opal glass necessitates an alteration in the usual course of analysis, since not only has the estimation of phosphoric acid to be considered, but also the removal of the phosphoric acid from the respective solutions, before the estimation of the alkalis and metallic oxides present can be carried out.

The phosphoric acid is estimated by decomposing a sample by means of hydrofluoric and sulphuric acids. The temperature employed for this decomposition must be regulated so as not to drive off any of the sulphuric acid, but only to remove all the fluorine as silicon fluoride and as hydrofluoric acid; otherwise phosphoric acid may be lost by volatilisation. The residue is dissolved in nitric acid, diluted and filtered, and the phosphoric acid in the filtrate determined by the molybdate method.

For the estimation of the alkalis a portion is decomposed with hydrofluoric and sulphuric acids, and after dissolving the residue in hydrofluoric

acid, ferric chloride and ammonium acetate solutions are added and the whole boiled to remove the phosphoric acid as basic ferric phosphate. After filtering off the precipitate the filtrate is treated in the usual way for the separation of the alkalis from the metallic oxides and for the removal of the sulphuric acid.

The silica is separated from the portion fused with sodium carbonate by decomposition and evaporation with nitric acid. In case lead oxide or any other metallic oxide precipitated by sulphuretted hydrogen is present in the filtrate, these must be previously removed and the phosphoric acid separated either by acetate and carbonate of lead or by nitrate and carbonate of silver according to the usual methods. After the filtration of the precipitate the excess of the precipitants is removed by sulphuretted hydrogen or hydrochloric acid respectively. The resulting solution, free from phosphoric acid, is then further treated as described.

The precipitated silica always retains a small quantity of phosphoric acid, almost the whole of which can be removed by treating the filtered and washed precipitate with aqueous ammonia; a little silica is however dissolved by this treatment, which is separated by adding a little nitric acid to the ammoniacal solution, evaporating to dryness, dissolving the residue in water with a little nitric acid and filtering off the separated silica, which is added to the main portion.

**6. Coloured Glass.**—The great variation in the chemical composition of different kinds of coloured glass necessitates differences in the methods of analysis adopted. The nature and number of decompositions necessary and the general course of analysis depend partly on the colouring substances present but chiefly on the nature of the glass, whether lead-free or lead glass, borate or phosphate glass, etc.; accordingly the most suitable method described above under these headings is selected.

The decomposition of coloured glass by fusion with sodium carbonate can be undertaken without any risk in a platinum crucible even if the glass contains easily reducible metallic oxides such as tin, antimony, or lead oxides, because by using an oxidising flame there is no likelihood of any reduction taking place. In the decomposition with hydrofluoric and sulphuric acids in the presence of tin and lead oxides a clear solution does not result on dissolving the evaporated residue either in hydrochloric or in nitric acid; if metallic compounds precipitated by sulphuretted hydrogen are present they must be removed from the solution for the estimation of the alkalis by passing in sulphuretted hydrogen before the further treatment of the liquid is proceeded with. This must always be done when the metallic oxides are not removed from the solution by the subsequent precipitant (ammonium carbonate and calcium hydroxide); in some cases this may involve a precipitation with ammonium sulphide.



The separation of the silica is carried out in the usual way. Whether hydrochloric or nitric acid is used for this purpose depends upon the nature of the metallic oxides present; in the presence of tin or antimony oxide nitric acid is not applicable, because meta-stannic acid and antimonious acid would be formed, which would remain mixed with the silica. The separation and estimation of the metallic oxides in the filtrate follows the ordinary analytical course and usually offers no difficulties. To estimate very small quantities of colouring agents such as gold in ruby glass, a separate decomposition with hydrofluoric acid of at least 5 g. of substance is made.

In glass containing antimony it is difficult to completely separate antimony oxide from the silica even by repeated boiling with hydrochloric acid containing tartaric acid. The following somewhat complicated method has been found satisfactory, as the result of a series of experiments.

A sample of the finely powdered glass is fused with from four to five times its weight of sodium carbonate, the melt softened with hot water either in a beaker or porcelain basin, and after decomposition with hydrochloric acid evaporated to dryness on the water-bath. Hydrochloric acid and water are then added, the vessel covered with a clock-glass, heated for thirty minutes on the water-bath, and the silica filtered off; the filtrate is again evaporated to dryness to separate the last traces of silica, which are collected with the main portion and washed. The still moist and impure silica is next washed from the filter paper into a platinum basin and the residue adhering to the paper removed by washing with hot sodium carbonate solution and finally with hot water; an 8 per cent. solution of sodium carbonate is then added in such quantity that about 18 to 20 c.c. are present for each 0.1 g. of silica. The solution is boiled until the silica is completely dissolved, and whilst covered with a clock-glass acidified with hydrochloric acid, added by means of a pipette; heating is continued until no more carbon dioxide is evolved and the silica then separated by two successive evaporations when it is obtained quite pure. The antimony oxide and any lead oxide previously admixed with the silica are present in the filtrate as chlorides, from which they can be separated by means of sulphuretted hydrogen.

**7. Glass Enamels, Metallic Enamels and Enamel Colours.**—Glass in the broader sense includes the various enamels used for the protection or decoration of metals, and for the ornamentation of glass vessels, and also the enamel colours employed for the decoration of glass and earthenware. The great diversity in the chemical composition of these materials renders it impossible to give detailed methods for their examination; the following observations and the qualitative examination indicate the course to be adopted.

Gold, silver, and copper enamels, which come into commerce in the form of flat discs, are more or less easily fusible, lead-flint glass of various colours, mostly containing boric acid. Opaque enamels are usually coloured by means of arsenious or tin oxide. They are examined by the methods used for coloured glass and for borate and flint glass respectively.

Iron enamels are generally lead-free, but contain boric acid and often fluorine. The coating of enamel fused upon sheet iron or cast iron goods almost always consists of two layers; the lower is a blue-grey ground-enamel and the upper a white opal enamel coloured by oxide of tin or a true coloured enamel. The latter must always be separated for the quantitative examination and are analysed by the methods for glass containing boric acid and fluorine.

To determine whether the enamel of a cooking utensil contains lead, a small piece of filter paper moistened with hydrofluoric acid is placed upon the enamel and allowed to remain for some minutes; the paper, together with any pasty mass adhering to the enamel, is then washed off into a small platinum basin, diluted with water, and tested for lead by means of sulphuretted hydrogen.

Opaque or transparent glass enamels for the decoration of glass articles, which are applied in a thick, pasty coating and then burnt in, usually come into commerce in the form of powders, less frequently in pieces. They consist of varieties of glass rich in lead, and sometimes contain boric acid; they melt very easily, and in the state of powder are completely decomposed by dilute hydrochloric or nitric acid, which considerably simplifies their examination.

Enamel colours, also called glass or porcelain colours, used for the decoration of glass and earthenware and which, in contrast to enamels, are applied only in comparatively thin coatings, usually consist of a fire-proof colouring material intimately mixed with an easily fusible glass and the so-called flux. Since the flux, which is rich in lead or boric acid, is always decomposable by acids, whilst the colouring material is mostly unaffected, the examination of enamel colours is considerably simplified. A fusion with sodium carbonate is unnecessary, and should also be avoided on account of any injurious effect on the platinum crucible.

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## CALCAREOUS CEMENTS

By CARL SCHOCH, Ph.D., Royal Technical High School, Berlin. English translation revised by Walter F. Reid.

THE raw materials of the calcareous cement industry are compounds of calcium, which occur in nature mainly as calcium carbonate in the form of limestone, chalk, etc., and as calcium sulphate in the form of gypsum. Next in importance to these main ingredients come magnesium carbonate, in the form of dolomitic limestone, and the various puzzuolanas. The latter, which may be either natural or artificial, are not in themselves capable of forming cements, but render burnt and slaked lime hydraulic when mixed with it.

Artificial cements of the class of Portland cement are prepared by incorporating two or more materials; clay is a further raw material used in this branch of the industry.

### I. LIME

#### A. LIMESTONE

Limestones adapt themselves, according to the amount of clay they contain, to the production of:—Quicklime, hydraulic lime, and Roman cement; this last lacks the property of being slaked by water, and has to be comminuted by grinding by machinery.

Apart from admixtures derived from clay, such as silica, alumina, and ferric oxide, almost all limestones contain as minor constituents, magnesium usually as magnesium carbonate, organic matter (bitumen and carbon), and moisture. Pyrites and alkalis also occur, and more rarely phosphoric acid and manganous oxide.

As a rule, these substances are only present in minute amounts or traces. There are, however, some limestones which contain several per cent. of pyrites, and others with almost 2 per cent. of carbon; a limestone from Saxony (Berggiesshübel) and another from Venezuela, both examined by Schoch, contained from 1 to 2 per cent. of anthracite. Magnesium carbonate may be present in even greater quantity; it tends to raise the hardness and specific gravity of dolomitic limestone.

## I. PRELIMINARY TESTS

**Gas-volumetric determination of the Calcium Carbonate.**—This is carried out volumetrically by decomposing the finely powdered limestone with hydrochloric acid in a closed vessel and collecting the evolved carbon dioxide in a measuring tube. In this operation small amounts of magnesium carbonate of course escape detection, but amounts greater than 4 to 5 per cent. and upwards are easily recognised. On decomposition by hydrochloric acid magnesium carbonate evolves its carbon dioxide far more slowly than calcium carbonate; hence if, after the first evolution, as read off on the measuring tube, a gradual further increase of volume be noted, the presence of over 3 per cent. of magnesia is indicated with certainty. The apparatus used for the decomposition is known as the calcimeter.

The following three forms of calcimeter are the most suitable and efficient:—

1. The Lunge and Marchlewski apparatus and the simplified modification of Lunge and Rittener, neither of which require the use of tables. They have been already described on pp. 149 and 153 respectively.

2. The Scheibler-Dietrich apparatus.

3. The Baur-Cramer apparatus, as modified by Schoch.

The two latter calcimeters are constructed and manipulated as follows:—

The Scheibler-Dietrich apparatus (Fig. 149) consists of two tubes connected by means of thick-walled rubber tubing. The tube *a* is graduated from 0 to 200 c.c., and is held fixed by two clamps; the other tube, *b*, slides up and down upon an upright and serves as a levelling tube. A 1 per cent. solution of boric acid in previously boiled water is used as the confining liquid. The measuring tube is contracted at the upper end and is provided with a three-way stopcock, *d*, through which connection can be made either to the air, or through *c* to the generating vessel.

Since the graduation of the tube *a* extends to 200 c.c., twice the quantity of substance indicated in the subjoined table should be weighed out, and the resultant reading divided by two.

The apparatus is tested before use by lowering the levelling tube *b*, when the liquid should remain at a constant level.

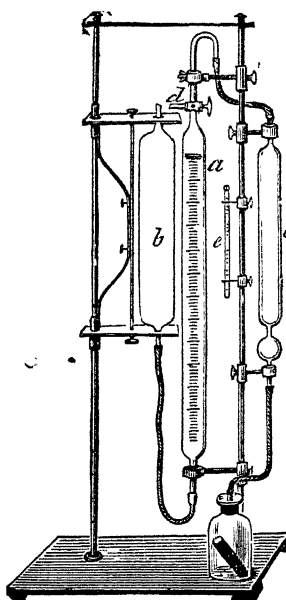


FIG. 149.

To carry out a determination the barometer and thermometer are read, and the amount of substance to be weighed out then found by referring to the subjoined table; for instance, at  $12^{\circ}$  and 765 mm. pressure  $2 \times .4250 = .8500$  g. is weighed out. The powdered substance is introduced into the generating vessel, together with a small tube containing 5 c.c. of hydrochloric acid of sp. gr. 1.124. The vessel is closed by the rubber stopper, the liquid in *a* set to zero, and connection established between the generating flask and the measuring tube by means of the stopcock *d*. By tilting the generating flask the acid is then brought into contact with the limestone, and as the liquid in *a* is forced down, equilibrium is established by lowering the levelling tube *b*. When the

evolution of gas has ceased, the apparatus is allowed to cool for three minutes, the levels adjusted, and the meniscus in *a* read off. Half the figure thus obtained represents the percentage of calcium carbonate.

It is to be noted that a small portion of the carbon dioxide is retained in solution in the generating flask. This absorption factor can only be determined by direct experiment with a given apparatus, and must always be added to the volume of gas read off.

The Baur-Cramer apparatus (Fig. 150) has undergone numerous modifications. Its original form was much improved by Cramer, who adopted petroleum as the confining liquid. Experiments by Schoch have, however, shown that petroleum also absorbs carbon dioxide, and that a solution

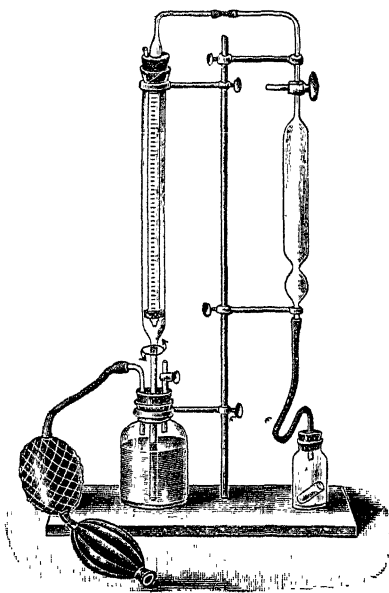


Fig. 150.

of boric acid slightly tinged with litmus is preferable. The original form of generating vessel was also found to be inconvenient and difficult to clean, and the apparatus was therefore assimilated somewhat to the Scheibler-Dietrich form, the only difference being that instead of two tubes standing side by side, the measuring tube is contained within the levelling tube; this is the only surviving feature of the original Baur apparatus. The measuring tube is graduated from 0 to 100 c.c., or, for special use with cement, from 50 to 100 c.c. Instead of using a levelling tube, equilibrium is established by opening a stopcock at the bottom of the outer tube and letting out water until the levels in the two tubes coincide, otherwise the manipulation is similar to that of the Scheibler-Dietrich apparatus.

Table of the Weight of Substance to be Weighed out,  
when 1 c.c. of carbon dioxide represents 1 per cent. of calcium carbonate, for barometric pressures of  
from 720 to 770 mm. and for temperatures from 10° to 25° C.

Temp. ° C.	MILLIMETRES.														
	720	722	724	726	728	730	732	734	736	738	740	742	744		
10°	0.4033	0.4044	0.4055	0.4067	0.4078	0.4090	0.4101	0.4112	0.4124	0.4135	0.4146	0.4158	0.4170		
11	0.4015	0.4026	0.4038	0.4049	0.4060	0.4072	0.4083	0.4094	0.4106	0.4117	0.4128	0.4140	0.4151		
12	0.3997	0.4008	0.4020	0.4031	0.4042	0.4054	0.4065	0.4076	0.4087	0.4099	0.4110	0.4121	0.4132		
13	0.3979	0.3991	0.4002	0.4013	0.4024	0.4036	0.4047	0.4058	0.4069	0.4080	0.4092	0.4103	0.4114		
14	0.3961	0.3973	0.3984	0.3995	0.4006	0.4017	0.4029	0.4040	0.4051	0.4062	0.4074	0.4085	0.4096		
15	0.3943	0.3954	0.3965	0.3977	0.3988	0.3999	0.4010	0.4021	0.4032	0.4044	0.4055	0.4066	0.4077		
16	0.3925	0.3936	0.3947	0.3958	0.3969	0.3980	0.3992	0.4002	0.4014	0.4025	0.4036	0.4047	0.4058		
17	0.3906	0.3918	0.3929	0.3940	0.3951	0.3962	0.3973	0.3984	0.3995	0.4006	0.4017	0.4028	0.4039		
18	0.3888	0.3899	0.3910	0.3921	0.3932	0.3943	0.3954	0.3965	0.3976	0.3987	0.3998	0.4009	0.4020		
19	0.3869	0.3880	0.3891	0.3902	0.3913	0.3924	0.3935	0.3946	0.3957	0.3968	0.3979	0.3990	0.4001		
20	0.3850	0.3861	0.3872	0.3883	0.3894	0.3905	0.3916	0.3927	0.3938	0.3949	0.3960	0.3971	0.3982		
21	0.3831	0.3842	0.3853	0.3864	0.3875	0.3886	0.3897	0.3908	0.3919	0.3929	0.3940	0.3951	0.3962		
22	0.3812	0.3823	0.3834	0.3844	0.3855	0.3866	0.3877	0.3888	0.3899	0.3910	0.3921	0.3932	0.3942		
23	0.3792	0.3803	0.3814	0.3825	0.3836	0.3847	0.3857	0.3868	0.3879	0.3890	0.3901	0.3912	0.3922		
24	0.3772	0.3783	0.3794	0.3805	0.3816	0.3826	0.3837	0.3848	0.3859	0.3870	0.3881	0.3891	0.3902		
25	0.3752	0.3763	0.3774	0.3785	0.3796	0.3806	0.3817	0.3828	0.3839	0.3850	0.3860	0.3871	0.3882		

Table of the Weight of Substance to be Weighed out—Continued.

Temp. ° C.		MILLIMETRES.												
		746	748	750	752	754	756	758	760	762	764	766	768	770
10°	0.4180	0.4192	0.4203	0.4214	0.4226	0.4237	0.4248	0.4260	0.4271	0.4282	0.4294	0.4305	0.4317	
11	0.4162	0.4173	0.4185	0.4196	0.4207	0.4219	0.4230	0.4241	0.4253	0.4264	0.4275	0.4286	0.4298	
12	0.4144	0.4155	0.4166	0.4177	0.4189	0.4200	0.4211	0.4222	0.4234	0.4245	0.4256	0.4267	0.4279	
13	0.4125	0.4137	0.4148	0.4159	0.4170	0.4182	0.4193	0.4204	0.4215	0.4227	0.4238	0.4249	0.4260	
14	0.4107	0.4118	0.4130	0.4141	0.4152	0.4163	0.4175	0.4186	0.4197	0.4208	0.4220	0.4231	0.4241	
15	0.4088	0.4099	0.4110	0.4122	0.4133	0.4144	0.4155	0.4166	0.4177	0.4188	0.4200	0.4211	0.4222	
16	0.4069	0.4081	0.4092	0.4103	0.4114	0.4125	0.4136	0.4147	0.4158	0.4169	0.4181	0.4192	0.4203	
17	0.4050	0.4061	0.4072	0.4083	0.4095	0.4106	0.4117	0.4128	0.4139	0.4150	0.4161	0.4172	0.4183	
18	0.4031	0.4042	0.4053	0.4064	0.4075	0.4086	0.4097	0.4108	0.4120	0.4131	0.4142	0.4153	0.4164	
19	0.4012	0.4023	0.4034	0.4045	0.4056	0.4067	0.4078	0.4089	0.4100	0.4111	0.4122	0.4133	0.4144	
20	0.3993	0.4004	0.4015	0.4025	0.4036	0.4047	0.4058	0.4069	0.4080	0.4091	0.4102	0.4113	0.4124	
21	0.3973	0.3984	0.3995	0.4006	0.4017	0.4028	0.4039	0.4050	0.4061	0.4072	0.4082	0.4093	0.4104	
22	0.3953	0.3964	0.3975	0.3986	0.3997	0.4008	0.4019	0.4030	0.4041	0.4052	0.4062	0.4073	0.4084	
23	0.3933	0.3944	0.3955	0.3966	0.3977	0.3988	0.3998	0.4009	0.4020	0.4031	0.4042	0.4053	0.4064	
24	0.3913	0.3924	0.3935	0.3945	0.3956	0.3967	0.3978	0.3989	0.3999	0.4010	0.4021	0.4032	0.4043	
25	0.3893	0.3904	0.3914	0.3925	0.3936	0.3947	0.3958	0.3968	0.3979	0.3990	0.4001	0.4012	0.4022	

**Volumetric determination of the Calcium Oxide or Carbonate.—**

The calcium oxide or carbonate in a limestone can also be determined by titration. For this purpose 1 g. of the powdered substance is weighed into a flask, covered with a little water, and decomposed by the gradual addition of 25 c.c. of normal hydrochloric acid (*cf.* p. 86), cochineal being used as indicator. The liquid is then boiled to drive off carbon dioxide and after cooling titrated back with  $N/2$  ammonia or with normal sodium hydroxide solution; if methyl orange is used as indicator, the solution need not be boiled. The number of c.c. of normal acid required are simply multiplied by 5 or by 2.8 to give the percentage of calcium carbonate or oxide respectively in the substance.

When a limestone contains a notable amount of magnesia, the calcium and magnesium can be determined together by titration according to Newbury's method<sup>1</sup> with sufficient accuracy for technical purposes. This method is based on the facts that magnesium hydroxide is sufficiently soluble in water to colour phenolphthalein, and that, when boiled in dilute solution with sodium hydroxide, magnesia is completely precipitated and separated from calcium oxide. Half a gram of the limestone under examination is weighed into a conical flask of about 500 c.c. capacity, fitted with a rubber stopper and a thin-walled glass tube about 75 cm. long, which serves as a reflux condenser. Sixty c.c. of  $N/5$  hydrochloric acid are then added from a burette, the condenser inserted, and the liquid boiled gently for about two minutes, care being taken that no vapours escape. The tube is rinsed with a little water and removed, and the flask cooled under the tap; 5 to 6 drops of phenolphthalein solution (1 g. in 200 c.c. of alcohol) are then added, and the solution titrated to a faint pink colour with  $N/5$  sodium hydroxide. It is important to hit the point at which a slight pink tinge suffuses the liquid, even if it be transitory, for if alkali be added until a decided permanent coloration is formed the lime will come out too high. The volume of acid employed may be called "first acid," and that of alkali required "first alkali."

In the case of limestones containing insignificant amounts of magnesia this completes the determination, and:—

$$a \text{ c.c. acid} - b \text{ c.c. alkali} \times 2 \times 0.56 = \% \text{ CaO.}$$

In this case the solution need not be cooled, and a permanent coloration sets in at the moment of neutralisation.

**Determination of Magnesium Oxide.**—To determine magnesia, the process is continued as follows:—The neutralised solution is poured into a large test-tube of 30 cm. length and  $2\frac{1}{2}$  cm. bore furnished with a mark at a volume of 100 c.c. To the boiling liquid  $N/5$  sodium hydroxide is gradually added, c.c. by c.c., the boiling being repeated after each

<sup>1</sup> *Tonindustrie-Zeit.*, 1903, 27, 833.



addition, until a strong red coloration persists on continued boiling. With a little practice, this point can be easily judged to half a c.c. The alkali thus added to the neutralised liquid may be called "second alkali." Next, the liquid is made up to 100 c.c., boiled for a moment, and allowed to stand until the precipitate has settled. When this has taken place, 50 c.c. of the clear supernatant liquid are withdrawn with a pipette, and titrated back with  $N/5$  acid until colourless. The volume of acid required is multiplied by 2 and called "second acid." The calculations are then as follows:—

$$\text{Second alkali} - \text{second acid} \times 2 \times 0.40 = \% \text{ MgO.}$$

$$\text{First acid} - (\text{first alkali} + \text{second alkali} - \text{second acid}) \times 2 \times 0.56 = \% \text{ CaO.}$$

The excess of alkali used in precipitating the magnesia should be not more than 1 c.c.; hence the "second acid" should not exceed 1 c.c., otherwise the magnesium hydroxide carries down some calcium hydroxide.

This method tends to give too high results for magnesia and too low for lime. This is partly due to the formation of calcium carbonate, owing to the action of atmospheric carbon dioxide during the separation of magnesia. By the use of a large test-tube, as prescribed, this source of error is reduced to a minimum. Again, too little lime may be found when the calcium occurs in the limestone in the form of compounds such as feldspar, which are not decomposed by dilute acids. All alkalimetric methods are subject to this defect; nor does the calcimeter indicate lime in this form. Notable quantities of insoluble lime only occur very rarely in limestone.

Much soluble alumina and ferric oxide, if present, somewhat obscure the end-reaction in the first and second titrations. When alumina is precipitated by sodium hydroxide, however, the red coloration does not appear until all the alumina has come down; hence the proportion of magnesia found is not increased by the soluble alumina present.

The method described above is thoroughly serviceable for fairly pure materials, according to experiments carried out in the Tonindustrie laboratory. It does not give such good results for calcareous marls. This is not exclusively due to the presence of a little lime in the form of silicates insoluble in dilute acid. In the second titration with sodium hydroxide the bulk of the precipitate, which consists largely of insoluble matter, has a very disturbing effect, because the end-reaction is more difficult to recognise; the coloration must be unmistakably deep red. In the case of limestones containing much silica, alumina, and ferric oxide, the volume of liquid will exceed 100 c.c., and it is therefore well to use a more capacious measuring vessel from the beginning.

**Determination of Clay.**—When the calcimetric or alkalimetric method shows that much clay is present in a limestone, it is advisable

to determine the proportion of argillaceous matter, at any rate, with sufficient accuracy for technical work. For this purpose 2 g. of the powdered limestone (marl) are weighed into a round-bottomed porcelain dish of about 14 to 15 cm. diameter, which is half-filled with distilled water, and about 10 c.c. of hydrochloric acid are added. The dish is covered with a watch-glass and the liquid boiled for about ten minutes. Any sesquioxide of iron or of aluminium which may have gone into solution is then precipitated by ammonia, and the whole filtered through a smooth filter paper. The residue is washed three or four times, partially dried, separated carefully from the filter, and fully dried in a platinum crucible at a low red heat. The results are quite satisfactory to within about  $\frac{1}{4}$  per cent.; the time occupied by the determination is from one and a half to two hours.

## 2. COMPLETE ANALYSIS

In a complete analysis of limestone the following determinations are required:—Loss on ignition, which includes water, carbon dioxide, carbon and bitumen; silicate, comprising silica, alumina, and ferric oxide; calcium, magnesium, and sulphuric acid. In some cases the separate estimation of water and of carbon dioxide is desirable, whilst in the purer limestones, *i.e.* those containing about 4 to 5 per cent. of total silicates, it is unnecessary to estimate silica, alumina, and ferric oxide separately. This latter separation is only required in limestones of over 5 per cent. silicate content, and is frequently asked for in hydraulic limes. Exhaustive analyses of this kind will be discussed later in connection with cement and clay.

For an examination as specified above the first step is to collect a good average sample on the spot, which should preferably be done by the analyst personally. An untrained man only very rarely succeeds in drawing really representative samples. The superficial layer of stone in the quarry should be first hewn away, since it may be weathered, and a fairly large sample taken from the material lying behind or beneath.

**Moisture.**—If it is desired to determine the natural moisture, the sample must be immediately enclosed in an air-tight, glass receptacle and the determination made with the least possible delay.

About 100 g. of the stone are weighed out and placed in a wide glass tube, through which dry air is drawn at the ordinary temperature by means of a filter pump; the loss in weight gives the "Natural Moisture."

When the weight of the substance has become constant, the moisture of the air-dried material is determined by placing it in an air-bath (Thörner's air-bath, which is lined inside with porcelain, is to be recommended) and heating it for about two hours to 105°. When

the estimation of moisture is considered superfluous, the limestone can be dried directly on an iron plate.

**Loss on Ignition.**—Two g. of the dried substance, are weighed into a platinum crucible and ignited, to determine water, carbon dioxide, carbon and bitumen. The flame of the burner is raised gradually, during about fifteen minutes, to a maximum, and then kept at full height for another fifteen minutes. The crucible is then ignited for thirty minutes more over a blowpipe or over a high temperature burner; this ensures the removal of the last traces of carbon dioxide. The covered crucible is then allowed to cool for from ten to fifteen minutes and weighed; it should not be allowed to stand longer, since its contents, after ignition, are very hygroscopic. The ignited substance is then transferred from the crucible to a capacious porcelain dish, covered with a little water, and decomposed by hydrochloric acid for the estimation of the undecomposed matter, silica, etc.

To determine the separate components of the loss on ignition, the water is first determined by mixing 10 g. of the substance with lead peroxide and heating the mixture in a tube of refractory glass, through which a current of dry air is passed to carry off the water, which is retained in a weighed calcium chloride tube.

**Carbon Dioxide.**—The carbon dioxide is most simply determined by Mohr's well-known apparatus. This consists of a small flask of about 75 c.c. capacity provided with a doubly bored rubber stopper fitted with a funnel closed by a pinchcock, and a small calcium chloride tube. A charge of 1 g. of substance is introduced and covered with a little water, the funnel filled with 10 c.c. of hydrochloric acid, and the whole weighed. The acid is then cautiously dropped in upon the substance until decomposition is complete, and the last trace of carbon dioxide expelled by gently warming the flask, preferably on a water-bath, to a temperature not exceeding 75°. The apparatus is allowed to cool and then weighed; the loss in weight  $\times 100$  gives the percentage of carbon dioxide.

This method is only approximate, as the error is seldom less than  $\frac{1}{2}$  per cent. It is advantageous, therefore, to conduct the estimation of carbon dioxide simultaneously with that of water, by passing the current of air through potash-bulbs containing 1:3 potassium hydroxide solution, which are weighed before and after the experiment.

For an exact analysis the determination of the carbon dioxide should certainly be carried out by the gravimetric method of Fresenius-Classen, or by the gas-volumetric method of Lunge and Marchlewski (p. 149), or that of Lunge and Rittener (p. 153), since the method described above is altogether too untrustworthy (Lunge).

**Undecomposed Matter (Clay and Sand), Silica, Alumina, and Ferric oxide.**—The porcelain dish containing the solution of the ignited

sample in hydrochloric acid is half-filled with distilled water, the contents heated to boiling, and treated with ammonia, whilst still boiling, until the reaction is distinctly alkaline. The dish is then immediately removed from the flame and the contents stirred, when the precipitate settles rapidly. The whole is filtered, without decanting, into a litre flask, and the precipitate washed until no trace of ammonium chloride remains, as shown by testing with silver nitrate. The filter and precipitate are introduced, whilst still wet, into a platinum crucible, burnt, and ignited over a Bunsen flame for about ten minutes.

The contents of the litre flask are allowed to cool completely, made up to the mark, and thoroughly shaken. Two portions of 500 c.c. each are then taken for the determination of the calcium and magnesium and of the sulphuric acid respectively.

**Calcium.**—The first portion of 500 c.c. is acidified with hydrochloric acid in a 1000 c.c. beaker and heated to boiling. The acid is added in order to prevent a precipitation, in ammoniacal solution, of calcium carbonate, which is very apt to run through the filter. Whilst the liquid is boiling, the calcium is precipitated by adding solid oxalic acid, 3 parts of crystallised acid being used for each part of calcium oxide (theory requires 2.25 parts); any magnesium present must be included in the calculation, because calcium oxalate being somewhat soluble in magnesium chloride solution, it is necessary to convert all the magnesium present into magnesium oxalate.

The approximate percentage of calcium and magnesium oxides is rapidly and easily ascertained by the preliminary calcimetric test, so that it is possible to effect the precipitation with very nearly the exact quantity of oxalic acid required. The precipitation must, however, be carefully carried out, for if the whole charge of oxalic acid were added at once to the boiling liquid, it might boil over. It is best to add the reagent crystal by crystal, and to stir with a glass rod, during the addition; as soon as all the oxalic acid has been introduced, ammonia is added in slight excess, and the beaker allowed to stand overnight, preferably in a warm place.

Schoch has found, as the result of many hundred parallel experiments, that this mode of effecting the precipitation renders the double precipitation which is so often recommended unnecessary. The average error was less than  $\frac{1}{10}$  per cent. Moreover, if this method be properly carried out, there is no danger of the precipitate passing through the filter.

On the following day, or after at least three hours, the calcium oxalate is filtered off and washed with cold water until no trace of ammonium chloride remains. The filter and precipitate are then carefully removed to a platinum crucible and burnt wet. After igniting for

half an hour over the blast, the calcium oxalate is completely converted to calcium oxide.

**Magnesium.**—The filtrate from the calcium oxalate is made slightly acid with hydrochloric acid and evaporated to about 200 c.c.; the addition of acid prevents the separation of magnesium salts. The liquid is then transferred to a 600 c.c. beaker, allowed to cool, treated with  $\frac{1}{2}$  of its volume of 25 per cent. ammonia, and sodium phosphate added, which precipitates the magnesium as magnesium ammonium pyrophosphate; the precipitate requires at least twelve hours to settle out completely. After this interval it is filtered off and washed with water containing  $\frac{1}{2}$  of its volume of ammonia. In testing the washings with silver nitrate, a just visible bluish-white opalescence indicates sufficient washing. The precipitate is then dried upon the filter, separated from it as far as possible, the filter incinerated in a coil of platinum wire and added to the main precipitate in a small porcelain crucible, which is ignited, after adding a few drops of nitric acid if necessary, until the contents are quite white. A second ignition, or even ignition over the blast, may be required. No black specks should remain in the precipitate, but a bluish-grey tinge is without effect on the result. The results tend to come out from  $\frac{1}{10}$  to  $\frac{2}{10}$  per cent. too high.

This method for the separation and estimation of calcium and magnesium is in use, and gives satisfaction, in most of the cement laboratories in Germany. Other methods are described in the section on "Sodium Sulphate and Hydrochloric Acid" (p. 406) and also under the analysis of cement (p. 693). T. W. Richards' work (*cf.* p. 406) deals with the objections that have been raised against the method by some workers who contend that a portion of the magnesium comes down with the calcium precipitate, and by others who hold that a little calcium goes over into the magnesium filtrate.

**Sulphuric Acid.**—For this estimation the second 500 c.c. of the filtrate from the insoluble matter are used.

In the case of a limestone containing visible admixtures of pyrites, the usual manner of preparing the sample for analysis must be modified, by first drying it at 105°, but without igniting. Two g. are weighed into a capacious porcelain dish, covered at once with bromine water, and decomposed by adding from 25 to 30 c.c. of hydrochloric acid, little by little, the dish being kept cool; all the sulphur liberated as sulphuretted hydrogen is thus oxidised without loss. After complete decomposition has taken place, the liquid is filtered and the total sulphur determined in the filtrate as on p. 274.

In order to determine sulphur and sulphuric acid separately, two analyses are made, side by side, the one as above and the other without bromine water. These give respectively the total sulphur and the

sulphur existing as sulphuric acid; the difference represents sulphur present as sulphide.

#### B. QUICKLIME

Burnt lime absorbs water and carbon dioxide from the air with great avidity; hence samples, to be of any value, should be taken at the kiln, and should be put into bottles and hermetically sealed at once. Small fragments should be rejected in sampling; it is best to break up large pieces and to take the samples from the centre.

The complete chemical analysis of lime is carried out exactly like that of limestone. A simple method for the estimation of the free lime and carbon dioxide, devised by Lunge, is described on p. 483. The determination of the loss on ignition should not be omitted, since water and carbon dioxide are apt to be taken up in spite of every care.

The technical valuation of quicklimes, more especially for building purposes, includes:—

1. Keeping properties.
2. Slaking power.
3. Increase of volume on slaking.

**1. Keeping Properties.**—These do not bear so much on the quality of the lime as such, as on the practical requirements of storing and transporting. It is useful to know how long a lime will keep before slaking and falling to powder by atmospheric agencies; the longer this period, the better for the lime-burner, since it can be kept in stock longer and can be sent to greater distances.

**2. Slaking Power.**—Hard-burnt, white lime, on treatment with water, should slake quickly and completely with evolution of heat.

If the treatment with water be limited in duration and quantity (*e.g.*, the lime be dipped in water for one to two minutes, until just soaked), dry calcium hydroxide is formed, and the lime crumbles gradually to an impalpable powder of specific gravity 2.08. If the lime be allowed to stand for some time with much water (as in mortar-making), it eventually swells to a stiff paste. The latter process is the usual one in the building trade.

The slaking power of lime is of great importance in several industries. Thus it is imperative for makers of slag-cement and of artificial stone to know how soon a given lime slakes, in order that they may modify the slaking process accordingly, and avoid getting unslaked lime into the mixings. This might happen owing to incomplete slaking, and might lead to subsequent hydration in the finished product, causing swelling, and rendering the goods useless.

To estimate the slaking power Schoch uses Stiepel's lime-calorimeter, described on p. 483. In a long series of experiments he found that this instrument does not always satisfactorily fulfil its primary purpose

of indicating the content of quicklime in a lime. In many examinations of limes, some of which were very pure, it proved a failure, in so far as the slaking proceeded very slowly and allowed much of the evolved heat to escape unrecorded. On the other hand, the rate of the rise in temperature was found to be a trustworthy factor for ascertaining the exact time required for slaking. By using this apparatus, therefore, the artificial-stone maker has a simple means of judging how long and how strongly he must slake his lime in order to obtain a fully hydrated product.

**3. Increase of Volume on Slaking.**—The swelling which takes place on slaking lime is more or less marked, according to the purity and density of the sample.

Since the sale of lime is now conducted more and more by weight, the determination of the increase of volume on slaking has been correspondingly simplified; the mortar-volumenometer designed by Michaëlis (Fig. 151) is used for this purpose.

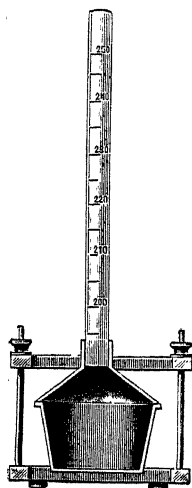


FIG. 151.

This apparatus is convenient in use, easily manipulated, and sufficiently accurate; its dimensions, however, ought to be greater, allowing for a charge of 100 g. of lime, instead of only 50 g. It consists of a brass receptacle of exactly 400 c.c. capacity, upon which a graduated glass tube can be tightly screwed; the graduation proceeds upwards from 200 to 300 c.c. For the estimation, a piece of lime weighing exactly 50 g. is placed in the brass vessel, and water, say 120 c.c. for the first experiment, added; the correct amount of water can only be gauged by several trials. In testing hydraulic lime, 100 g. are taken and 200 c.c. of water added. The vessel is at once covered with a watch-glass and warmed on the water-bath, the contents being shaken down from time to time by smartly knocking the vessel upon the bench; as soon as the paste begins to crack it is cooled and the lid and tube screwed on; 200 or 300 c.c. of water, as may be required, are then added from a pipette, and the volume of the lime cream read off.

The weight of a litre of normal lime cream varies from 1350 g. to 1450 g.

If the volume, and not the weight, of the original lime is to be taken as basis, the piece of lime weighing 50 g. is quickly dipped into molten paraffin wax, and the volume determined. The increase of volume on slaking is from 3.0 to 4.5. The determination of volume by bushel measures is altogether untrustworthy.

The quantity of water which a lime takes up on conversion into

dry or pasty hydroxide varies greatly, and is mainly conditioned by its degree of purity. In place of the direct estimation of the slaking increment described above, an indirect method was proposed by Stingl, in which the quality of a lime is determined by measuring its capacity for water. The weight of water required by a known quantity of lime of sp. gr. 2.3 to form a paste of definite consistency is ascertained, and the specific gravity of this paste then taken. By the aid of these two data the increase of volume can be calculated. This method has the defect of introducing the doubtful quantity, "a paste of definite consistency," which is not easily estimated in the case of thin creams. Again, the method requires much more time and trouble than the mortar-volumenometer. The joint investigations of Tetmajer, Hauenschild, and Michaëlis go to prove that the consistency of a lime paste is not a simple function of its water-content.

The standard consistency of lime paste is provisionally defined as that at which when cracks just begin to appear with Rüdgersdorf lime, a piston of the Vicat needle type (Fig. 152), weighing 2 kilos, penetrates to a depth of 25 mm. Rüdgersdorf lime is accepted as the standard for this test in Germany; there is no corresponding standard in this country. The manipulation of this instrument is quite simple, and is evident from the illustration.

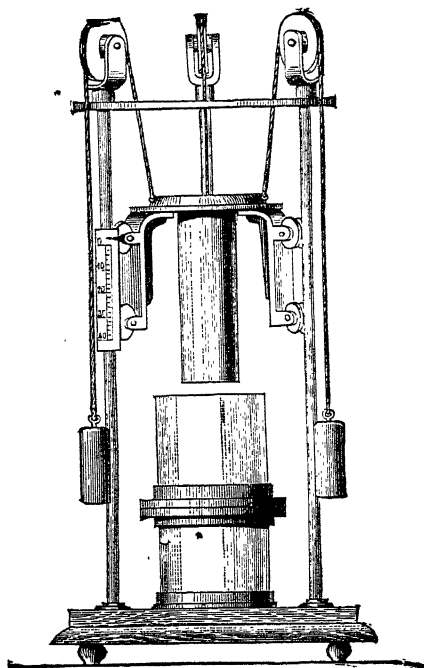


FIG. 152.

### C. LIME

The tensile strain test, which will be described in detail under cement, is an important factor in the valuation of lime. The test should be carried out more especially upon mixtures containing varying amounts of sand; the usual proportions of sand are 3, 4, and 5 parts to 1 part of lime. It is customary in practice to make up these mixtures by volume. For accurate work this is, of course, inadmissible; even mixtures by weight of lime paste and sand are not sufficiently definite. The more recent and better method is to make up mortars of so many parts by weight of sand to one part by weight of the solid



lime contained in the lime cream or paste (of standard consistency) used. The starting point is thus the ignition-residue of the lime paste, which should be about one-third of the whole.

The breaking strains attained by lime mortar are not very considerable; with a good lime the following results may be expected after twenty-eight days :—

Breaking strain with	3	4	5 { parts of Sand.
By tension—Kilos per sq. cm.	3 to 4	4 to 5	3.5 to 4.5
Lbs. per sq. in.	43 to 57	57 to 71	50 to 64
By compression—Kilos per sq. cm.	9 to 16	12 to 20	10 to 18
Lbs. per sq. in.	128 to 227	170 to 284	142 to 256

It is well to examine the test pieces for porosity by Michaëlis's method, which is described under "Portland Cement" (p. 712).

**Determination of Lime in Mortar.**—In the case of large buildings the mortar is sometimes mixed in a central factory, and delivered to the builders. In order to find out whether such mortars contain the right proportion of lime, methods have been devised by Frühling and by Holmblad, both of which are easily carried out and yield useful results.

*Frühling's Method.*<sup>1</sup> This method depends upon the rapid decomposition of ammonium salts by calcium hydroxide. A hollow cube of zinc, open at opposite ends, of exactly 100 c.c. capacity is placed on a smooth surface and completely filled, avoiding crevices, with the mortar under examination. The excess of mortar at the top of the cube is scraped away. The contents of the cube are then introduced through a metal funnel into a stoppered bottle, and the residues clinging to the cube and funnel washed down with 150 c.c. of ammonium chloride solution. The funnel is then removed, the bottle closed and violently shaken for some time, until the mortar and the solution are intimately mixed. The bottle is allowed to stand, still stoppered, for about fifteen minutes, whilst the sand settles out from the lime dissolved in the solution. The supernatant liquid need not become perfectly clear; any bulky flakes remaining suspended have no serious effect upon the subsequent testing. One hundred c.c. of the decanted liquid are then measured off, poured into a porcelain dish previously half-filled with 400 to 500 c.c. of water, and coloured a full red with about twenty drops of an alcoholic solution of rosolic acid. The dish is then placed under a 200 c.c. burette charged with hydrochloric acid of such strength that 1 c.c. = 0.05 g. CaO, and titrated, with constant stirring, until the red colour changes to a faint yellow. The number of c.c. used correspond exactly to the kilos of lime contained in 1 cubic metre of the mortar.

<sup>1</sup> *Tonindustrie-Zeit.*, 1884, 8, 393.

Unmixed slaked lime can be similarly assayed, if a known volume or weight be treated as above. The experimental error is not more than about  $\frac{1}{2}$  per cent.

*Holmblad's Method*<sup>1</sup> is simpler and easier than that of Fröhling. The strength of the hydrochloric acid is so adjusted that 1 c.c. neutralises 0.05 g.  $\text{Ca(OH)}_2$ , and therefore indicates 1 per cent. of lime. The measuring vessel in which the sample is taken has a cubic capacity corresponding to 5 g. of mortar with 14 per cent. of water. Thus the weight of dry mortar contained in it is,  $5 \times 0.86 = 4.3$  g. This percentage of water is the average proportion for mortar, and small divergencies on either side do not seriously affect the result.

The apparatus consists of three parts, the sampling vessel, the testing jar, and the acid-bottle. The sampling vessel is a small brass cylinder closed at one end and fitted with a movable piston. The testing jar is a graduated glass cylinder, on which each division represents 0.86 c.c., that is, 1 per cent. of lime upon the dry mortar. The acid-bottle is of the usual dropping-bottle type.

To carry out a test, the sampling vessel is filled with mortar and emptied by aid of the piston into the testing jar. Water is then added up to the zero mark, the stopper inserted, the jar thoroughly shaken, and rosolic acid added; the contents are then ready to receive the acid.

If it can be assumed that the mortar contains not less than 5 or 6 per cent. of slaked lime, acid may be poured into the jar directly from the acid-bottle up to the fifth or sixth division. When this has been distributed in the liquid by shaking, the red colour due to the rosolic acid becomes evident. The addition of acid is then continued drop by drop until, on shaking, the red colour is changed to a dirty yellow. The lime is thus neutralised, and the percentage of slaked lime is given by the level of the liquid. Average mortar contains from 8 to 10 per cent. of lime.

The only drawback of this very simple method is that the hydrochloric acid neutralises any grains of calcium carbonate which may have been present in the sand, so that the lime content of the mortar comes out too high. By proceeding cautiously, however, the free calcium hydroxide can always be observed to undergo neutralisation first.

To eliminate this source of error entirely, it is safer and quite as rapid to adopt Lunge's method (*cf.* p. 483), which, when carried out with care, is not affected by the presence of calcium carbonate. The indicator employed is phenolphthalein.

A simple method has been worked out in the Tonindustrie laboratory<sup>2</sup> for the determination of the lime in lime-sand mixtures, as a control of the mixings in the manufacture of artificial stone. The sample for analysis is preferably drawn from the wet paste in the mixing

<sup>1</sup> *Tonindustrie-Zeit.*, 1889, 13, 143.

<sup>2</sup> *Ibid.*, 1902, 26, 1719.

machinery or pug-mill. It is usually advisable, however, to drive the paste through a sieve by aid of a stiff brush, so as to effect an even distribution of the lime. To estimate the latter, 100 g. of paste are weighed into a stoppered bottle, which, after the addition of 25 g. of ammonium chloride, is half-filled with water and thoroughly shaken. About 20 drops of phenolphthalein are then added, which impart a red colour to the liquid, and the bottle is again shaken. Fifty c.c. of hydrochloric acid of known strength are then cautiously added; the red colour of the liquid disappears temporarily, but reappears on shaking. As long as the red coloration remains, there is still free lime present. On adding more acid, c.c. by c.c., with thorough agitation, the colour is slower in returning after its initial disappearance, and the addition of acid is then continued in portions of 0.5 c.c. at a time. Finally, when a wine-red tinge only appears after standing for five minutes, the neutralisation may be regarded as complete. The sand stirred up by the shaking does not hinder the recognition of the end-reaction, as it settles rapidly, leaving the colour evident in the supernatant liquid. The whole operation is completed in a few minutes. When the change of colour is definitely effected as above, the number of c.c. of hydrochloric acid used is read off and divided by 10, which gives the lime content directly, assuming that 100 c.c. of acid contain 12.8 g. of HCl, equivalent to 10.0 g. of CaO.

For the testing of milk of lime, Blattner<sup>1</sup> has published a table of specific gravities (see p. 484), by the use of which the lime content can be determined hydrometrically.

Or the amount of lime contained may be estimated by titration with normal hydrochloric acid, whilst any calcium carbonate present is found by the method described on p. 666. Heavy residual matter, especially sand, is estimated by elutriation (cf. p. 689).

## II. HYDRAULIC ADMIXTURES

These comprise numerous substances which are added to ready-burnt lime in order to form a hydraulic mortar. These so-called hydraulifactors are mainly:

- A. Puzzuolana, Santorin earth, and trass.
- B. Granulated blast-furnace slag, etc.

### A. NATURAL PUZZUOLANAS: PUZZUOLANA PROPER, SANTORIN EARTH, AND TRASS

These substances are all of volcanic origin and consist of tufas found respectively at Puteoli, near Naples, and in Auvergne (France), at

<sup>1</sup> *Dingl. Polyt. J.*, 1883, 250, 464.

Santorin, one of the Cyclades, and in the Eifel. Their typical chemical composition is given in the following table:—

	Puzzuolana.	Santorin Earth.	Trass.
Water . . .	up to 12 %	4.29 %	3 to 12 %
Silica . . .	52 to 60	65.43	49 to 59
Titanic acid . . .	...	.69	...
Alumina . . .	9 to 21	15.01	10 to 19
Manganous oxide . . .	...	.50	...
Ferric oxide . . .	5 to 22	1.88	4 to 12
Ferrous oxide . . .	...	2.06	...
Calcium oxide . . .	2 to 10	2.84	1 to 8
Magnesium oxide . . .	up to 2	1.06	1 to 7
Alkalis . . .	3 to 16	7.61	3 to 10

It is characteristic of all the three varieties that they contain chemically combined water; indeed, Tetmajer values them as hydraulising additions to mortars according to the loss on ignition of the substance previously dried at 110°. When this chemically combined water is expelled by heat, the puzzuolana loses its value as a hydraulic factor almost completely. In investigating puzzuolanas, it is therefore necessary to pay attention to this factor, apart from the general chemical composition.

The following analyses of Puzzuolanas from various sources show the proportion of ingredients soluble in hydrochloric acid. The hydraulicity depends mainly upon this relation.

	Puzzuolana. Italy. (Rivot.)	Puzzuolana. Auvergne. (Rivot.)	Trass. Rhing. (Elsner.)	
Silica . . .	19.5	28.2	11.5	Soluble in hydrochloric acid.
Alumina . . .	9.7	2.0	17.7	
Ferric oxide . . .	6.5	21.8	11.8	
Calcium oxide . . .	8.0	9.0	3.2	
Magnesium oxide . . .	0.9	...	2.2	
Alkalis . . .	2.6	1.2	2.7	Insoluble in hydrochloric acid.
Silica . . .	32.7	25.0	37.4	
Alumina and Ferric oxide . . .	8.1	6.7	1.8	
Calcium oxide . . .	1.2	1.3	2.2	
Water and loss . . .	10.2	4.1	9.5	

Feichtinger<sup>1</sup> is of opinion that the hydraulising properties of Santorin earth are due to the presence of "free," *i.e.* reactive silica.

Lunge and Millberg,<sup>2</sup> however, in their investigations on this subject came to the conclusion that easily decomposed silicates, and not free silica, are the active substance in puzzuolanas, and that all these hydraulic factors (Santorin earth, puzzuolana, trass, etc.) contain no free amorphous silica, but that they do contain, besides refractory silicates,

<sup>1</sup> *Dingl. polyt. J.*, 1870, 197, 146.

<sup>2</sup> *Z. angew. Chem.*, 1897, 10, 428.

presumably inactive silicates of the nature of zeolites, which are dissolved by 30 per cent. potassium hydroxide solution even on the water-bath. It is desirable also, therefore, to determine the value of hydraulicising materials from this point of view.

For trass the following standard tests have been suggested.<sup>1</sup>

**1. Determination of Hygroscopic Water and of Water of Hydration (Loss on Ignition).**—Good trass consists of ground hydraulic tufa. In most cases the loss on ignition affords information as to whether a trass is prepared from hydraulic tufa of good quality.

A good sample should give at least 7 per cent. loss on ignition (*i.e.*, chemically combined water), but this estimation alone is not to be regarded as conclusive evidence of the value of a trass.

Trasses of  $5\frac{1}{2}$  to  $7\frac{1}{2}$  per cent. ignition loss are satisfactory, provided that they are up to the standard in tensile strength.

*Preparation of the Samples.* An average sample of about 20 g. of the trass to be examined is taken and triturated in a mortar until it passes through a sieve of 5000 meshes to the sq. cm., without leaving a residue.

In case the trass is supplied in the form of unground blocks of tufa, care must be taken that the first sample drawn (about 10 kilos) represents the best possible average, and that the lumps picked out are well mixed together.

The 10 kilos of lumps are first pounded in a mortar until all passes through a sieve of 10 meshes to the sq. cm. The sifted material is then thoroughly mixed, and 1 kilo taken and ground fine enough to pass a sieve of 60 meshes to the sq. cm. without residue. Of the resulting powder 100 g. are finely ground and passed completely through a sieve of 900 meshes.

*Determination of Hygroscopic Water.* To determine the percentage of mechanically retained water 10 g. of the trass, prepared as above, are filled into a stoppered weighing-bottle of at least 4 cm. diameter. The bottle, with the stopper taken out, together with the stopper, is dried in a drying oven, heated by boiling water and provided with ventilators, for three hours to about 98°. Care must be taken that the flame does not spread beyond the bottom of the oven and heat the door, as this would raise the temperature of the interior above that imparted by the boiling water, and also, that no aqueous vapour penetrates into the oven.

The bottle is then stoppered, transferred to a desiccator, allowed to cool, and weighed. The loss in weight is regarded as representing the hygroscopic water in the trass.

To obtain greater accuracy, it is necessary to dry at 98° until the weight of the residue is constant; for practical purposes, however, three

<sup>1</sup> Vorstand für Materialprüfungen der Technik, 1900.

hours' drying suffices, since the subsequent loss in weight only amounts to tenths of a per cent.

*Determination of the Loss on Ignition.* For this purpose the second 10 g. of the sample are weighed into a platinum or porcelain crucible and ignited, either for thirty minutes over the blowpipe, or for at least forty minutes in a Hempel or similar furnace. It is desirable to begin the heating of the trass, which contains both water and air, very gradually, raising it to a red heat only after from five to ten minutes. If it is heated too suddenly, the expelled steam and air carry away particles of trass, and the loss thus incurred is falsely attributed to the true ignition loss.

After ignition the crucible is taken up with hot tongs, immediately placed in a desiccator to cool, and the loss in weight is determined.

In calculating the water of hydration, the loss in drying is subtracted from the total loss on ignition. The difference is calculated in percentages of the dried trass, that is, on the trass less the hygroscopic water.

**2. Degree of Fineness.**—To gauge the degree of fineness the sieves commonly applied to cement testing are used, having 144, 900, and 5000 meshes to the sq. cm. respectively.

Trass ought to be ground as finely as possible, for the binding power of the material increases with the fineness. Under present conditions one is justified in demanding that the 900-mesh sieve shall retain not more than 25 per cent. and the 5000-mesh not more than 50 per cent.

One hundred g. of the powder, dried at 98° to 100°, are taken and are first sifted upon the finest mesh. The portion remaining on the sieve is weighed and screened through the next mesh, and so on.

**3. Needle Test.**—The powdered trass is tested in the condition in which it is delivered, but grains which fail to pass through the 144-mesh sieve should be rejected, as they are apt to vitiate the test. In case the trass is intended for overground building, it is well to conduct the test on air-hardened material.

A mixture of 2 parts by weight of trass, 1 part by weight of powdered slaked lime, and 0.9 to 1 part by weight of water is gauged at 15° to 18°, filled into ebonite boxes without a bottom, which are set on a sheet of glass, and smoothed over at the top. The boxes are at once immersed in water at 15° to 18°, and tested with the standard needle apparatus (*cf.* p. 706), after standing for two, three, four, and five days respectively, the load being determined at which the standard needle fails to make an impression on the cement.

If the trass cement is to be used at low temperatures, as in winter or in subterranean building, it is desirable to carry out a second series of tests at a corresponding temperature. In all cases the temperature of the water and of the air should be stated.

It is usual to specify, in practice, that after four days a Vicat needle loaded with 1 kilo shall at  $15^{\circ}$  penetrate not further than 5 mm. into the mortar, whilst after two days the latter should no longer receive an impression from the finger. Above  $15^{\circ}$  a greater load is specified, viz., at  $18\frac{3}{4}^{\circ}$ , 2 kilos, and  $22\frac{1}{2}^{\circ}$ , 3.25 kilos.<sup>1</sup>

The lime employed, pending the definition of a standard lime, should be as pure as possible, and should be prepared from marble.

**4. Tensile and Crushing Strength.**—Test pieces for tension and compression are prepared in the shapes commonly used in cement testing, from a mixture of 2 parts of trass, 1 part of powdered slaked lime, 3 parts of standard sand, and 0.9 to 1 part of water, and are beaten down with 150 strokes of a Böhme hammer (*cf.* p. 718). The test pieces for tension are taken out of the moulds twenty minutes after filling; those for compression twenty-four hours after filling.

All the test pieces are kept for twenty-four hours, after preparation, in a covered, zinc box filled with moist air, and are then allowed to harden for six and twenty-seven days respectively, under water at  $15^{\circ}$  to  $18^{\circ}$ . They are tested immediately after being taken out of the water.

It is now usually required that after twenty-eight days the lime trass mortar shall have a tensile strength of at least 12 kilos per sq. cm., and a crushing strength of at least 60 kilos per sq. cm.; the mean value of the six highest figures out of ten experiments is taken.

The preparation and gauging of the materials is carried out as follows:—

The powdered trass is taken as delivered, without further treatment.

The lime used is pure, freshly burnt, fat lime. Five kilos, of pieces of the size of a walnut, are enclosed in a wire gauge, and held under water at  $20^{\circ}$ , until no more bubbles are disengaged. The lime is then thrown into a zinc-lined wooden receptacle, kept covered for eight days, and passed through a sieve of 120 meshes to the sq. cm.; the coarse residue is rejected.

Properly slaked lime contains about 25 per cent. of water. It must be kept in air-tight jars if intended for future experiments.

For a standard sand, that used in cement testing is taken. In Great Britain the standard sand from Leighton-Buzzard should be used.

The mortar is mixed in the mixing machine (*cf.* p. 716) in such a way that the trass and powdered lime are first mixed in a bowl, given twenty turns of the mixing-machine, stirred up with the dry sand in a bowl, and finally given another twenty turns of the machine, the water being added at the first turn.

Besides the above standard tests, it is customary to determine the

<sup>1</sup> *Cf.* A. Hambloch, *Der rheinische Trass, u.s.w.*, Andernach, 1903.

bushel weight of the trass. The weight of a loosely heaped hectolitre should not exceed 94 kilos (59 lbs. per cb. ft.).

Most puzzuolanas are dark in colour; in the case of trass this coloration is an important means of distinction from the much lighter coloured, so-called "wild" trass, which forms a loose layer of volcanic ash upon genuine trass, and is practically destitute of hydraulic properties.

### B. ARTIFICIAL PUZZUOLANAS

Of the various materials which fall under this head, metallurgical by-products, especially granulated blast-furnace slag, have proved the most valuable.

In the valuation of such slags as hydraulifactors the following points are to be considered :—

The slag should be basic in the sense that the ratio  $\text{CaO} : \text{SiO}_2$  should be not less than unity; it should be as rich as possible in alumina, and should be as free as possible from manganese, magnesia, and sulphur (as calcium sulphide). A slag of good quality should approximate to the following composition :—

$\text{SiO}_2$	25 to 36 per cent.	$\text{CaO}$	30 to 50 per cent.
$\text{Al}_2\text{O}_3$	10 to 22 "	$\text{MgO}$	up to 3 "
$\text{Fe}_2\text{O}_3$	up to $1\frac{1}{2}$ "	$\text{CaSO}_4$	up to 2 "
$\text{FeO}$	up to 2 "	$\text{CaS}$	up to 3 "
$\text{MnO}$	up to 3 "	$\text{KNaO}$	... "

The determination of the loss on ignition is usually of little value, owing to the oxidations which take place in the process.

The analytical methods required for such products have been partially described under limestone (p. 658), and will be further dealt with under clay (p. 688).

It is essential to the good quality of the slag that the process of granulation should have been carried out at a white heat, at a high pressure, and with much water, at a temperature as near to freezing-point as possible.

The technical tests carried out with ready-mixed puzzuolanic and slag cements are in general similar to those for Portland cement (*cf. infra*). In addition the following data are specific in character :—

The proportions observed in mixing puzzuolanas and slags on the one hand, and lime on the other, are usually between 100 : 15 and 100 : 30; accordingly, the specific gravity of puzzuolanic and slag cements is about 2.7.

The colour of these materials varies from light grey to yellowish-brown.

In contrast with ordinary builder's mortar, the strength of these



cements is quite considerable even without the addition of sand; they are, as it were, self-contained mortars. The standard sand-strengths (1 part of cement to 3 parts of sand) of puzzuolanic cements, after seven days in the air and twenty-one days under water, are on the average:—

By Tension	{	6 to 16	kilos per sq. cm.
	{	85 to 227	lbs. per sq. in.
By Compression	{	30 to 100	kilos per sq. cm.
	{	427 to 1423	lbs. per sq. in.,

whilst those of slag cements reach 25 and 200 kilos per sq. cm. (356 and 2846 lbs. per sq. in.) respectively.

As these cements are artificial products, an important factor as regards their quality is the intimate intermixture of the ingredients, which is mostly a question of very fine grinding. A sieve of 900 meshes per sq. cm. should retain nothing at all, a sieve of 4900 meshes at most from 10 to 12 per cent.

Moreover, since the lime is worked in as slaked powder, tests should be made to ascertain whether it has been completely hydrated, and whether there are any residual granules of caustic lime. If such were present, they would undergo hydration in the finished product, greatly impair its strength, and lead to "blowing." Small quantities of unslaked lime do not affect a standard sand cement as used for testing, since they only fill up the hollow spaces in the first instance. Considerable quantities, however, set up tensions in the cement, which are manifested by distortion and cracking, and may eventually break up the test pieces altogether. Hence, it is particularly necessary, in examining puzzuolanic and slag cements, to test for permanency of volume. Faultless slag cements are absolutely permanent in volume under water and in air—that is, they retain permanently the shape into which they were moulded; also, they stand more severe tests than three hours' steam drying and three hours' boiling, without the least distortion or the formation of cracks of any kind.

Since most puzzuolanic and slag cements, however, set very slowly, tests of permanency, especially of the "accelerated" type, should not be made until setting is complete.

### III. HYDRAULIC CEMENTS

#### A. NATURAL HYDRAULIC CEMENTS

Hydraulic cements are distinguished as natural and artificial, according as they are obtained by merely calcining a naturally occurring mineral, or by working up two or more materials.

The former are subdivided into :—

1. Hydraulic lime.
2. Roman cement.
3. Dolomitic or magnesian cement.

The chief representative of artificial hydraulic cements is Portland cement, including ferruginous Portland cement.

## I. HYDRAULIC LIME

Hydraulic lime and Roman cement are closely related, the one shading almost imperceptibly into the other.

To ascertain whether a given product is hydraulic lime or Roman cement, the fact is taken advantage of that the former slakes and crumbles to some extent on treatment with water, whilst the latter does not slake, but has to be ground to a fine powder before use. This property is in the main dependent upon a smaller or greater admixture of clay, which, however, does not offer a decisive criterion in all cases. In any case, a chemical analysis of the material is indispensable in order to gain information as to the proportion of clay present. A simple calcimetric estimation of the calcium carbonate, or a determination of the carbon dioxide by Mohr's apparatus, does not afford sufficient data for valuation, since a sound product may be dolomitic, in which case other methods of analysis are necessary.

In the chemical analysis of this class of lime the determination of total silicate, *i.e.*, silica, alumina, and ferric oxide, is inadequate; the three constituents must be separately determined. Hence the method of analysis differs somewhat from that applied to ordinary lime.

### The Analysis of Hydraulic Lime.

The loss sustained by the substance, dried at  $105^{\circ}$ , on ignition is first determined, as in the case of ordinary limestone (p. 666), and the residue decomposed with hydrochloric acid. Hydraulic limes generally give an ignition loss of 10 per cent. The liquid is then evaporated to complete dryness on the water-bath, and well stirred with a glass rod when it begins to thicken, so that a loose, crumbly mass is ultimately produced. The porcelain dish and contents are placed in a drying oven and heated to  $110^{\circ}$  to  $115^{\circ}$  for at least two hours, whereby the hydrochloric acid is expelled and the silica rendered insoluble.

**Silica and Gangue.**—The dried mass is allowed to cool, moistened with hydrochloric acid, and left for several hours, preferably overnight. The dish is then half-filled with distilled water, warmed on the water-bath, and the liquid filtered direct into a litre flask which, after cooling, is filled up to the mark.

If the residue is of a pure white colour, free from sand, and not gritty when rubbed with a glass rod, it may be burnt wet; care is necessary in the ignition as the silica is extremely light and apt to fly off as dust. The filter is then incinerated, the crucible ignited for seven or eight minutes over the blowpipe, and weighed.

If, however, the silica is tinged yellowish-grey and contains sand, a separation of soluble (*i.e.* chemically active) and insoluble, inactive, or sandy silica is necessary. For this purpose the precipitate and filter are returned to the porcelain dish and heated with the addition of 200 c.c. of a 10 per cent. solution of anhydrous sodium carbonate for about an hour on the water-bath. The soluble silica is thus completely dissolved, and the inactive silica or sand remains behind. The residue is washed by decantation with hot water, again treated with hot sodium carbonate solution, and filtered. The residue on the filter consists of sand and gangue, and is burnt wet; the united filtrates, which contain all the soluble or active silica, are acidified, evaporated to dryness, and again dried at  $110^{\circ}$  to  $115^{\circ}$  for two hours. The dried mass is moistened with strong hydrochloric acid, allowed to stand overnight, washed by decantation and on the filter with hot water, and weighed.

Alkali hydroxide cannot be used in place of carbonate, Lunge and Millberg<sup>1</sup> having proved that inactive quartzose silica is markedly attacked by the former (*cf.* p. 585).

The original filtrate from the silica and sand contained in the litre flask is withdrawn by a pipette in three quantities of 400, 300, and 300 c.c. respectively, into beakers of 800 and 600 c.c. capacity. The 400 c.c. are used for estimating the sesquioxides, calcium, and magnesium, the first 300 c.c. for estimating the alumina and ferric oxide separately, and the second 300 c.c. for estimating the sulphuric acid.

**Sesquioxides.—Alumina and Ferric Oxides.**—The 400 c.c. of the above solution are boiled with a few drops of nitric acid, in order to oxidise any ferrous oxide present, and the iron and alumina precipitated in the boiling solution by the addition of a very small excess of ammonia, free from carbonate. The ammonia is added drop by drop until the liquid becomes reddish-brown, *i.e.* approaches neutralisation, and the precipitation then effected by the addition of a small extra quantity of ammonia (*cf.* pp. 582 and 610). A considerable excess of ammonia would tend to redissolve alumina. It is not necessary to add ammonium chloride before precipitating, unless much magnesia is present. After precipitation, the beaker is removed from the flame, the precipitate allowed to settle, filtered off with the least possible delay, and washed on the filter with hot water, care being taken that the precipitate is well stirred up by the washing. If this precaution is not observed, the glutinous alumina is apt to choke the pores of the paper and render

<sup>1</sup> *Z. angew. Chem.*, 1897, 10, 333; *cf.* p. 585.

filtration tedious; for the same reason the precipitate should on no account be left unwashed on the filter paper for any length of time, say overnight. After washing, the filter is burnt wet in a platinum crucible, ignited, and weighed as  $\text{Al}_2\text{O}_3 + \text{Fe}_2\text{O}_3$ ; too strong ignition should be avoided, since the ferric oxide might be partially converted into ferroso-ferric oxide.

**Calcium and Magnesium.**—These are determined in the filtrate from the sesquioxides by the methods detailed on p. 405 *et seq.* and p. 667 *et seq.*

**Separation of Alumina and Ferric Oxide.**—In the second aliquot part (300 c.c.) of the filtrate from the silica, iron is determined by the method given on p. 380.

**Ferrous Iron.**—Should it be desirable to determine the iron present in the ferrous as well as that in the ferric condition, 2 g. of the original substance, dried at  $100^\circ$  but not ignited, are decomposed in a flask by sulphuric acid in a current of carbon dioxide. The turbid solution is washed into a 400 c.c. flask, previously charged with about 1 g. of sodium bicarbonate, filled up to the mark, and well shaken. After settling, 200 c.c. are withdrawn and titrated with potassium permanganate, to determine the FeO. The remaining 200 c.c. are filtered, completely reduced by means of zinc, and again titrated with permanganate, whereby the percentage of  $\text{FeO} + \text{Fe}_2\text{O}_3$  is ascertained.

**Sulphuric Acid.**—The third portion of the filtrate from the silica is used for the determination of the sulphuric acid, which is carried out as described on p. 668.

**Bitumen.**—Occasionally the material under examination is highly bituminous, and it is then advisable to determine the bitumen; this can only be done with accuracy by a combustion, as with an organic substance.

The above analytical determinations merely show how much clay is present in the lime; they do not serve to differentiate the material into hydraulic lime or Roman cement, nor do they give a definite indication as to its value.

The contained clay is effective only when it is evenly distributed throughout the mineral, instead of occurring, as sometimes happens, in the form of pockets. Limestones of the latter character give much trouble in burning, and afford a very heterogeneous product.

**The Examination of Marls** for hydraulic qualities has been fully investigated by Lunge and Schochor-Tscherny,<sup>1</sup> who proceed as follows:—

The coarsely powdered material is ignited for two hours at a white heat, finely powdered, and boiled, first with dilute hydrochloric acid (1 : 3) and then with 5 per cent. sodium hydroxide solution. The two solutions thus obtained contain all the chemically active silica and silicates; the

<sup>1</sup> *Z. angew. Chem.*, 1894, 7, 481.

residue, consisting of inactive silica, is dried, ignited, and weighed. The percentage of the latter may be regarded as a negative indication of quality: the lower the proportion, the better the quality of the marl.

**Differentiation of Hydraulic Lime and Roman Cement.**—To decide whether a given material is hydraulic lime or Roman cement, the only possible means is by comparative experiments in slaking; considerable practice is required for this test. The trials are made with hot water and in covered vessels, so as to utilise the heat of combination as fully as possible. Hydration frequently sets in briskly only when a piece of fat lime is slaked and laid under the lumps of hydraulic lime—a case, apparently, of contact action.

Hydraulic limes, when wetted, crumble to hydroxide to a greater or less extent. Small lumps which refuse to fall to powder may be due to nodules of clay, or sand, or pebbles embedded in the lime. Sand and pebbles deteriorate the quality of hydraulic lime; nodules of clay, on the other hand, may, if crushed and well mixed with the hydrated powder, actually enhance its value as a hydraulic cement.

When a hydraulic lime forms a homogeneous body, its value is mainly dependent upon the percentage of silica. The noted "chaux du Theil" consists almost entirely of calcium silicate practically free from alumina and ferric oxide.

Minerals of this character, whilst excellent sources of hydraulic lime, are not so well adapted to the manufacture of cement, since their high proportion of silica is apt to cause violent disintegration of the clinker.

Finally, a satisfactory decision as to the value of a hydraulic lime can only be arrived at by means of the technical tests for permanency of volume and tensile strength.

The strength of hydraulic lime, without admixture, is fairly low. Also, its capacity for sand is less than that of quicklime, and mortars mixed in the proportion 1 : 5 are almost always inferior in strength to 1 : 3 mixtures.

The after-hardening is very considerable; it continues for two years or more, and strengths of 30 kilos per sq. cm. (427 lbs. per sq. in.) by tension and 250 kilos per sq. cm. (3558 lbs. per sq. in.) by compression may then be reached.

The time of setting of hydraulic limes varies greatly. As a rule it is about from twenty to thirty hours, but it has been known to be only three to four hours in some cases, and as much as ten days in others.

**Permanency of Volume.**<sup>1</sup>—Hydraulic lime cements scarcely ever show signs of blowing in the air. Under water, however, this occasionally happens, as the result of the belated hydration of granular

<sup>1</sup> Cf. Tetmajer, *Methoden und Resultate der Prüfung der hydraulischen Bindemittel*, vol. vi., 1893.

inclusions, such as over-burnt lime, or insufficiently hydrated particles of marl.

The ordinary test by water takes too long to be of practical use. Permanency of volume can, however, be readily and quickly determined by using water or moist air at 50°. Either test is satisfactory, and much to be preferred to dry heating. The test for permanency of volume must never, of course, be carried out until the test pieces have thoroughly set.

## 2. ROMAN CEMENT

Roman cements are distinguished from the limes hitherto treated of, by refusing to slake and needing artificial comminution before they can be applied as cements. In chemical composition, also, they differ from true hydraulic limes in containing more clay.

The analytical examination of Roman cements is conducted exactly as in the case of hydraulic or ordinary lime. The percentage of clay is such that it bears to the percentage of lime the ratio from 1 : 1.2 to 1 : 1.6. This figure, viz., the proportion of lime to total silicate, is known as the "hydraulic modulus."

The following is an average analysis of Roman cement:—

Silica . . . . .	up to 27 per cent.
Alumina . . . . .	8 to 10 „
Ferric oxide . . . . .	3 to 6 „
Calcium oxide . . . . .	48 to 59 „
Magnesium oxide . . . . .	up to 3 „
Sulphuric acid . . . . .	up to 2 „
Alkalis . . . . .	up to 1 „

If the chemical composition of a given material lies within these limits, it is fairly certain that the article is of good quality, but its real value can only be decided by the mechanical tests for setting, permanency of volume, and strength.

In examining the raw material from which Roman cement is made, homogeneity of chemical composition is an important criterion of quality, inasmuch as the stone goes straight into the kilns; an artificial adjustment of the quality, as in the case of Portland cement, is excluded.

Since Roman cement must be ground before use, the fineness of the powder should be determined, as the strength of the mortar made from it increases with the degree of fineness. Roman cement is not burnt to incipient fusion, that is, not to maximum density, and consequently the calcined product retains its looseness of texture, and the ground powder is comparatively soft and impalpable.

Roman cements may be defined as products obtained by calcining

argillaceous marls below the point of incipient fusion, so that they do not slake with water, and have to be powdered mechanically.

The specific gravity varies between 2.7 and 3.0; it very rarely exceeds the latter. The loss on ignition is 5 per cent. or less. Its colour is yellowish to reddish-brown.

Roman cements absorb water and carbon dioxide with avidity, and must therefore be kept, before testing, in air-tight vessels, as otherwise they deteriorate in quality.

As a rule they set with tolerable rapidity; incipient hardening is observed with rapid-setting cements in seven minutes, with medium setting cements in fifteen minutes or less, and with slow-setting cements in upwards of fifteen minutes. The time of setting is determined as in the case of Portland cement (p. 706).

Roman cements must permanently keep the shape in which they have hardened. A cake of cement which has been placed under water twenty-four hours after gauging or setting should show no cracks or distortions whatever after twenty-eight days' immersion.

Besides these standard tests, which take up much time, certain accelerated tests have come into use. These comprise especially the hot-water test at 75° and the steaming test at 75°; tests carried out at 100°, as with Portland cement, as also the ignition test, are not always satisfied, even by the best of Roman cements. Accelerated tests should last for six hours, and should be commenced twenty-four hours after gauging, and certainly not before setting is complete. Should the test pieces fail in the 75° tests, another series should be carried out at 50°.

The degree of fineness of Roman cements should be high; at least 64 per cent. of the powder should pass through a sieve of 2500 meshes to the sq. cm., and at least 82 per cent. through a 900-mesh sieve.

The binding power and strength of Roman cement is tested by tension and compression, as detailed under Portland cement. In the normal mortar of one part of cement to three parts of sand, a good material should, after seven and twenty-eight days—the first twenty-four hours in moist air, the remainder under water—attain the following minimum breaking strains:—

	Days.	Tension.		Compression.	
		Kilos per sq. cm.	Lbs. per sq. in.	Kilos per sq. cm.	Lbs. per sq. in.
Rapid-setting cements . . {	7	4	57	...	...
	28	8	114	60	854
Medium and slow-setting cements {	7	5	71	...	...
	28	10	142	80	1138

The actual strength of the best sorts of Roman cement exceed these minimum figures very considerably; their breaking strains may reach 20 kilos and 180 kilos per sq. cm. (284 and 2562 lbs. per sq. in.) after twenty-eight days. Secondary setting generally proceeds for a year

or so, and strengths approaching 30 kilos and 300 kilos per sq. cm. (427 and 4270 lbs. per sq. in.) by tension and compression respectively, are then attained.

The strength of unmixed Roman cement also is high compared with that of hydraulic lime; the tensile strength after seven days is 12 to 15 kilos, after twenty-eight days 20 to 30 kilos per sq. cm. (171 to 213 and 284 to 427 lbs. per sq. in.).

### 3. DOLOMITIC OR MAGNESIAN CEMENT

When a limestone contains a considerable amount of magnesium carbonate, it is called "dolomitic." Pure dolomite is a mixture of calcium and magnesium carbonates,  $\text{CaCO}_3 + \text{MgCO}_3$ , and has the composition  $\text{CaCO}_3$  54.3 per cent.,  $\text{MgCO}_3$  45.7 per cent. A pure dolomite of this character is, however, by no means the best for cement making; dolomites with from 8 to 10 per cent. of clay are more suitable, for the following reason. In calcining dolomitic limestone the temperature must not rise above  $400^\circ$ , because only magnesium carbonate and no calcium carbonate loses its carbon dioxide below this temperature. If any considerable quantity of quicklime were formed, the resulting product would crumble, when exposed to water, to a loose mass of poor consistency, and the strength of the cement would be greatly impaired. In this connection the clay exerts a favourable influence, as it hydraulifies any quicklime that may be formed. Indeed, when the proportion of clay is inadequate, the material is hydraulified by a deliberate admixture of some puzzuolana such as brick-dust. Magnesia has the property of hardening under water in presence of calcium carbonate.

The value of a dolomitic raw material is tested, in the first instance, by chemical analysis. Minerals containing less than 10 per cent. of magnesium oxide are of inferior quality, whilst clay, up to 10 per cent. enhances their value.

The material should be experimentally calcined on the small scale, care being taken that all the magnesium carbonate is causticised, but only so much of the lime, if any, as will combine with the clay present. The burnt product is then used for the usual technical tests, viz., setting, permanency of volume, and strength. It must be ground fine, since it does not slake with water.

The setting period of dolomitic cement is moderate, from three to twelve hours. The colour very much resembles that of heavy hydraulic lime. Its specific gravity is about 2.7.

In strength, as also in other points, dolomitic cement stands midway between hydraulic lime and Roman cement. Schoch found, as the result of a number of tests, that a 1 : 3 cement-sand mixture had after twenty-eight days—seven days in air, twenty-one days under water—a mean



tensile strength of 12 kilos per sq. cm. (171 lbs. per sq. in.). With five parts of sand a strength of 9 kilos per sq. cm. (128 lbs. per sq. in.) was observed.

The strength of the unmixed cement is poor; on the other hand, this material stands a very considerable admixture of sand.

#### B. ARTIFICIAL HYDRAULIC CEMENTS. PORTLAND CEMENT, ETC.

Whereas all the cement materials hitherto considered are calcined and come into use in the condition of mixture in which they occur naturally, artificial hydraulic cements, of which Portland cement is the most important, are manufactured from two or more ingredients such as limestone, marl, clay, etc.

#### RAW MATERIALS

Of the raw materials used in the manufacture of artificial hydraulic cements, limestone and marl have already been dealt with as regards chemical analysis (p. 681 *et seq.*).

**Clay.**—The analysis of clay (*cf.* p. 568) is similarly carried out, except that on account of its being imperfectly soluble in hydrochloric acid, it must first be decomposed by fusion with alkali carbonates. For this purpose 10 g. of a mixture of fifty parts of potassium carbonate, fifty parts of sodium carbonate, and five parts of potassium nitrate, previously thoroughly mixed in a porcelain mortar, are weighed into a capacious, deep platinum crucible. The clay is finely powdered in an agate mortar, dried at 105°, 2 g. weighed out on a tared scoop, added to the fusion mixture, and thoroughly incorporated by means of a thick platinum wire. The resulting mixture should appear quite homogeneous, and should not reach more than half-way up the crucible, as spitting is apt to occur during the fusion. The crucible is then heated over a small flame, and the temperature very gradually raised. The contents of the crucible shrink together and ultimately, at a low red heat, form a cake with partially fused edges. The main decomposition of the clay by the alkali is effected at this stage, and the mass should be maintained in this condition for at least half an hour; it is then completely fused for about a quarter of an hour, and if necessary over the blowpipe. The crucible is allowed to cool, placed with its contents in dilute hydrochloric acid in a porcelain, or preferably platinum dish, digested on the water-bath, the solution evaporated to dryness on the water-bath, and the analysis conducted as with hydraulic lime. Should the melt be coloured greenish-blue, the presence of manganese is indicated; this can be determined by first precipitating the iron and aluminium together, in presence of sodium acetate, and then estimating the manganese in the filtrate as peroxide by means of bromine-water. The estimation of

the manganese is always necessary in the analysis of slags. The filtrate contains the calcium and magnesium, which are determined as described on p. 667 *et seq.*

The raw materials for the manufacture of Portland cement may vary widely in chemical composition, as there is considerable opportunity for adjustment in the manufacture. The most suitable materials are marls, in which either lime or clay may predominate, because they are more or less ready-mixed naturally; it is essential that the mixture should be uniform.

Chemical analysis alone does not decide as to the suitability of a clay in all cases. It is important that the clay should not contain too much magnesia or sulphuric acid or pyrites, since these may greatly affect the permanency of volume of the finished cement. How much a clay may contain cannot be definitely stated, as it depends upon how much magnesia and pyrites, if any, are present in the limestone, and on the proportion of clay material to limestone. It is safe, however, to pass 3 to 4 per cent. of magnesia and 2 to 3 per cent. of sulphuric acid in a clay.

Whilst chemical analysis affords information as to the content of magnesia and sulphur, it gives no clue as to the amount of quartzose or sandy silica present (*cf.* p. 585). Sand, especially when plentiful and of coarse grain, is mere ballast in slurry for Portland cement, since it goes unchanged through the kiln. This drawback can be avoided to a slight extent by grinding the raw materials exceedingly fine. As this involves an increased expenditure of power, attempts were formerly made to remove the sand by elutriation, but additional expense is incurred in this case also in eliminating the water thus introduced. It is preferable, therefore, either to reject very sandy clays or to expend a little more steam power on the grinding.

*Estimation of the Sand in Clay.* The sand in a clay is estimated by *Elutriation* (*cf.* p. 569). For this purpose 50 g. of the dried and coarsely powdered sample are weighed into a capacious porcelain dish, covered with water and crude hydrochloric acid in the proportion 3 : 1, and boiled for three hours. On cooling, the acid liquid is carefully decanted off and the residue further elutriated with water. This is most simply effected by allowing a gentle current of water to flow into the dish, whilst the solid matter is cautiously rubbed down with the fingers and the suspended clay allowed to escape by the lip of the dish until nothing but clear sand remains behind. This simple method has the advantage of effecting a ready and complete separation of sand and clay, whereas in the ordinary elutriating apparatus the only mechanical effect which comes into play is that of the stream of water, which is often inadequate. Sometimes the clay adheres so firmly to the sand that even heating with strong sulphuric acid or boiling with sodium hydroxide fails to

free the sand entirely from clay, and the action of gently flowing water must obviously be much less effective.

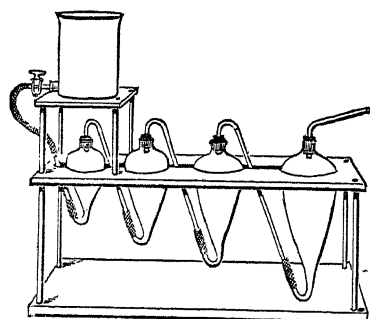


FIG. 153.

If it be preferred, however, to have recourse to an elutriating apparatus, either that of Nobel or of Schöne may be used.

Nobel's apparatus (Fig. 153) consists of a series of conical jars provided with an overflow tube at the upper end of each. The first vessel is connected with a reservoir of water, and the elutriation effected by placing the sample to be tested in this vessel and regulating the washing according to the rate of overflow.

Schöne's apparatus (Fig. 154) is rather more complicated, but not more accurate. Its main feature is the elutriating funnel, about 50 cm. long, which is provided with an inlet tube bent upwards. The upper end of the funnel is connected with an N-shaped piezometer tube, 100 cm. in length, which has a small circular hole at the apex of the downward bend. The mud having been placed in the funnel, a stream of water from the feed-tube E is made to traverse the funnel from below upwards. The only advantage of the apparatus is that the rate of flow, as represented by the pressure of the exits, can be accurately read off in the graduated tube. The elutriation can therefore be carried out at a definite and uniform pressure.

When the clayey matter has been completely separated from the sand by one of these methods, the latter is washed into a small porcelain dish and dried, first on the water-bath, and then in the oven.

In order to determine the degree of fineness of the sand either the dried sand may be sifted, or, using Schöne's apparatus, the sandy residue is elutriated at gradually increasing pressures and the several products determined separately.

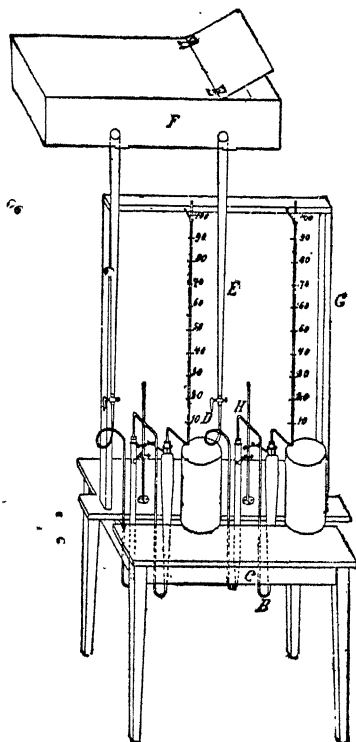


FIG. 154.

It is customary to distinguish the following grades:—

Silt : diameter of grain up to .025 mm. .

Dust : diameter of grain up to .040 mm.

Fine Sand : diameter of grain up to .200 mm.

Coarse Sand : diameter of grain above .200 mm.

So far as normal, marketable clays are concerned, chemical analysis affords fairly trustworthy data as to the cements which may be obtained from them.

Clays containing much combined or quartzose silica have the disadvantage that the cement clinker is very apt to dust, with the result that a poor cement is obtained unless the dusting be promptly arrested by sprinkling with water. The strength of these cements is but moderate shortly after setting; after hardening, however, it proceeds slowly but continuously for two years, and then only begins to fall off a little. The time of setting is protracted.

In contrast with highly siliceous cements, clays containing much alumina and carbonated or caustic alkalis produce exceedingly rapid-setting cements; the mechanical strength is less than in the case of slow-setting cements. This is explained by the fact that the particles of such cements have not time enough, within the short period of setting, to adhere closely to each other or to the grains of added sand. Clays with much alumina and alkali are specially used for the manufacture of quick-setting cements; they are not so highly burnt in the preparation.

Clays with a high proportion of gypsum or pyrites, on the other hand, form slow-setting cements, owing to the formation of alkali sulphates. Should the clay be deficient in sulphuric acid, an addition of gypsum is made to the finished cement, but not more than 2 per cent. should be added, since with a larger proportion many cements show a tendency to swell.

As regards the technical preparatory treatment of the raw materials, the chemical nature of the clay is again of importance, in so far as plastic clays require a low burning temperature and yield very firm bricks, whereas sandy clays, more especially when associated with a dense, hard limestone of great purity, afford a material of very low cohesion in moulding the slurry.

#### PORTLAND CEMENT

In the manufacture of Portland cement, limestone and clay are weighed out in definite proportions, ground together wet, and the slurry thus obtained moulded into bricks and calcined to incipient vitrification; the crushed and finely ground clinker constitutes Portland cement.<sup>1</sup>

<sup>1</sup> For details of the manufacture of cement, cf. *Calcareous Cements*, by G. R. Redgrave and C. Spackman, 1905; *Cements, Limes, and Plasters*, by E. C. Eckel, 1905; *Portland Cement*, by R. K. Meade, 1906; *Die moderne Aufbereitung der Mörtelmaterialien*, by G. C. Schoch.

**Chemical Analysis.**—The analysis of clinker or finished cement is carried out by Schoch precisely in the same way as that of clay, except that the initial fusion with alkali carbonates is unnecessary.

In the case of slurry, if the percentages of clay and limestone (or lime) only are to be determined, the scheme of analysis given for argillaceous limestones, marl, etc., under I. A. 2, p. 665 suffices. If, however, it is desired to estimate the several constituents present, as in cement or clay, it is necessary to decompose the substance by fusion with alkali carbonates; ignition alone, even on the most powerful blow-pipe, fails to render the material soluble in many cases.

On the basis of a series of analyses of cements and slurries, by various chemists, Hillebrand<sup>1</sup> has worked out the following standard scheme of cement analysis:—

Of the cement under examination 0.5 g. is weighed out into a platinum crucible and ignited for fifteen minutes over a powerful blowpipe. The sample is then decomposed by hydrochloric acid and the solution obtained filtered off from the insoluble residue; the latter is decomposed by fusion with sodium carbonate, the melt extracted with water, and the aqueous extract added to the main solution.

*Silica.* The solution is evaporated to dryness and the separated silica filtered off; the filtrate thus obtained is again evaporated and any further silica which may have separated collected. The two portions of silica are united, dried, ignited for thirty minutes over the blast, and weighed. The contents of the crucible are then evaporated down with 10 c.c. of hydrofluoric acid and four drops of sulphuric acid, ignited, and again weighed; the difference between the two weighings gives the  $\text{SiO}_2$ .

*Sesquioxides.* The filtrate from the silica is made alkaline with ammonia free from carbonate, the excess boiled off, and the precipitated hydroxides filtered off, washed once or twice, dissolved in hydrochloric acid, and reprecipitated by ammonia. After filtering and washing, the precipitate is ignited for ten minutes, and weighed.

The boiling off of any considerable excess of ammonia is apt to render the precipitated aluminium hydroxide slimy, and to cause difficulties in filtering and washing (*cf.* p. 610).

*Ferric Oxide.* In order to separate iron from aluminium, the ignited sesquioxides are fused in a platinum crucible with 10 g. of acid potassium sulphate and the melt extracted with hot water and dilute hydrochloric acid. Any silica still present is filtered off, the filtrate reduced by means of sulphuretted hydrogen, the excess of the latter driven off by carbon dioxide, and the iron estimated by titration with permanganate or by the method described on p. 582, which is less troublesome.

<sup>1</sup> *J. Soc. Chem. Ind.*, 1902, 21, 12 and 1221.

*Calcium Oxide.* The combined filtrates from the sesquioxides are boiled and the calcium precipitated with ammonium oxalate. After standing for a short time the precipitate is filtered off, washed, and gently ignited in a platinum crucible; it is then dissolved in hydrochloric acid, any alumina present precipitated by ammonia, the filtrate boiled, and the calcium again precipitated as oxalate. The precipitate is filtered off, ignited over the blowpipe, and weighed as  $\text{CaO}$  (cf. p. 405). As an alternative, the excess of oxalate used for the precipitation can be titrated back with permanganate and the content of calcium oxide calculated indirectly.

*Magnesium Oxide.* The two filtrates from the calcium are united, concentrated by evaporation, sodium phosphate added, the liquid boiled, then allowed to cool and ammonia added, at first drop by drop, and finally in excess. The precipitation is carried out in a flask, which is shaken from time to time to facilitate the separation of the precipitate. After standing for two hours the precipitate is filtered off, dissolved in dilute hydrochloric acid, and the precipitation repeated as before. The precipitate is finally ignited over the blast and weighed as  $\text{Mg}_2\text{P}_2\text{O}_7$  (cf. p. 406).

*Sulphuric Acid.* This is determined by dissolving 1 g. of the substance in hydrochloric acid, filtering, and precipitating the filtrate with barium chloride (cf. p. 274).

*Sulphur.* One g. of substance is fused with sodium carbonate and a little potassium nitrate, the melt extracted with hot water, the solution filtered, acidified, and precipitated with barium chloride.

There is no doubt that good results are obtained by this method of analysis; it is, however, questionable whether the several double precipitations are indispensable, as they render the analysis somewhat involved and tedious.

Schoch has compared the method with his own, and found no differences of any importance in the results, but he is of opinion that the weight of substance taken for analysis is too small; the maximum difference observed was about 0.127 per cent. The drying of the evaporated silica at  $110^\circ$  to  $115^\circ$  is certainly avoided, but a double determination of silica is thereby rendered necessary; also, he regards the double precipitation of calcium as superfluous, as by his own method calcium tends to come out too low rather than too high.

Stanger and Blount<sup>1</sup> advocate heating the evaporated silica to at least  $200^\circ$  for an hour. In this they seem to disregard the fact that ferric chloride becomes volatile at  $120^\circ$ . Hillebrand noted losses in silica up to 2 to 3 per cent. with this method of ignition.

Stanger and Blount also lay stress on the desirability of having quite a thin layer of substance on the dish in the drying operation,

<sup>1</sup> *J. Soc. Chem. Ind.*, 1902, 21, 1216.

which is certainly correct. They determine silica, sesquioxides, and calcium in separate portions of the sample. The filtrate from the calcium is evaporated with the addition of 40 to 50 c.c. of nitric acid of sp. gr. 1.4, and the ammonium salts are driven off by heating, for the determination of the magnesium. The residue thus obtained is dissolved in water and a little hydrochloric acid, and precipitated with sodium phosphate, after previously removing traces of silica, alumina, oxide of iron, or of calcium by the addition of a little ammonia and ammonium oxalate. The magnesium precipitate is burnt wet, a method which is certainly not in accord with general practice.

*Total Alkalis.* According to Herzfeld, 10 g. of cement are ignited over the blast, extracted when cool with water, and carbon dioxide passed into the aqueous solution in order to precipitate the calcium as carbonate; the filtrate is then made slightly acid with hydrochloric acid, evaporated to dryness, and neutral ammonium carbonate added. The liquid is again filtered, the filtrate carefully evaporated, the residue gently ignited in a platinum dish or crucible, and the mixed chlorides weighed.

*Sodium and Potassium.* The following method is recommended by W. Michaëlis. Two g. of the finely powdered substance are moistened with water in a platinum dish, strong sulphuric acid and hydrofluoric acid (1:20) added, the whole evaporated on the water-bath, and the excess of free acid cautiously expelled by heating. The residue is dissolved in hot hydrochloric acid, and the aluminium, iron, and calcium precipitated together by the addition of ammonia and oxalic acid. The filtrate is evaporated to dryness, the ammonium salts driven off, the residue dissolved in a very little water, about 20 c.c. of Schaffgotsch's solution (*cf.* p. 584) added, and the magnesium precipitate, after standing for twenty-four hours, filtered off and washed with about 30 c.c. of the same solution. The filtrate is evaporated to dryness, gently ignited, taken up with water, made slightly alkaline with ammonia, and again filtered. The only metals then in solution are the alkalis, as sulphates. The solution is rinsed into a platinum crucible, carefully evaporated, gently ignited, and the weight of  $K_2SO_4 + Na_2SO_4$  found.

The contents of the crucible are then dissolved in dilute hydrochloric acid, platinum chloride added, and the whole evaporated down to about 1 c.c. The sodium platinichloride formed is dissolved in a mixture of three parts of absolute alcohol and one part of ether, the insoluble potassium platinichloride filtered off and washed with the same mixture. The filter and precipitate are then burnt and gently ignited in a current of hydrogen, whereby the potassium platinichloride is reduced to metallic platinum. The contents of the crucible are transferred to a second filter paper, and washed with the least possible quantity of water; the potassium chloride is thus extracted and the

residual metallic platinum dried, ignited, and weighed. The weight thus obtained is calculated to potassium sulphate. The weight of sodium sulphate is obtained by difference, from that of the mixed sulphates.

The methods of estimating potassium used in the potash industry are described on p. 520 *et seq.*

*Magnesium Oxide.* Since a high percentage of magnesia throws suspicion of unsoundness upon a Portland cement, a separate estimation of magnesia is sometimes desirable. In this case the following procedure may be adopted. Two g. of the cement are decomposed with hydrochloric acid in a capacious porcelain dish, the solution diluted with water, heated to boiling, and the aluminium, iron, and calcium precipitated, together with part of the silica, by ammonia and ammonium oxalate. The liquid, including the suspended matter, is washed into a litre flask, cooled, made up to the mark, and thoroughly shaken. After settling, 400 c.c. of the clear solution are filtered off into a beaker, about 80 c.c. of ammonia added, and the magnesia precipitated as usual with sodium phosphate. The whole operation takes from two to three hours. After allowing to stand overnight the magnesium precipitate is filtered off and ignited; the results are correct to within 0.25 per cent. This method requires only twenty-four hours from start to finish, and is well adapted to the simultaneous testing of several samples.

**The Composition of Portland Cement.**—The chemical composition of a good Portland cement is confined within the following somewhat narrow limits:—

Silica . . . . .	19 to 26 per cent.
Alumina . . . . .	4 to 10 „
Ferric Oxide . . . . .	2 to 4 „
Calcium Oxide . . . . .	57 to 66 „
Magnesium Oxide . . . . .	up to 5 „
Sulphuric Acid . . . . .	up to 2 „
Alkalis . . . . .	up to 3 „

Any appreciable divergence from these figures is almost always accompanied by unsoundness and inadequate strength.

In the standard specifications of various countries and municipalities a certain maximum percentage is assigned to some of these constituents.<sup>1</sup> According to the British Standard Specification adopted by the Engineering Standards Committee<sup>2</sup> (1907), cement shall comply with the following conditions as to chemical composition:—“There shall be no excess of

<sup>1</sup> Cf. Redgrave and Shackman, *Calcareous Cements*, p. 275, Eckel; *Cements, Limes, and Plasters*, p. 614.

<sup>2</sup> *British Standard Specification for Portland Cement*, Publication No. 12, revised June 1907, issued by the Engineering Standards Committee, p. 6.

The Editor is indebted to the Engineering Standards Committee for their permission to include the data from their *British Standard Specification for Portland Cement*, and to reproduce the illustrations of the forms of apparatus recommended.



lime—that is to say, the proportion of lime shall not be greater than is necessary to saturate the silica and alumina present; this proportion shall not be greater than the ratio (calculated in chemical equivalents) represented by:—

$$\frac{\text{CaO}}{\text{SiO}_2 + \text{Al}_2\text{O}_3} = 2.85$$

(CaO = 56; SiO<sub>2</sub> = 60; Al<sub>2</sub>O<sub>3</sub> = 102).

The percentage of insoluble residue shall not exceed 1.5 per cent.; that of magnesia shall not exceed 3 per cent., and that of sulphuric anhydride shall not exceed 2.75 per cent.”

The quality and preparation of Portland cement is defined in the specification as follows:—“The cement shall be prepared by intimately mixing together calcareous and argillaceous materials, burning them at a clinkering temperature and grinding the resulting clinker. No addition of any material shall be made after burning, except when desired by the manufacturer, and if not prohibited in writing by the consumer, in which case calcium sulphate or water may be used. The cement, if watered, shall not contain more than 2 per cent. of water, whether that water has been added or has been naturally absorbed from the air. If calcium sulphate is used, not more than 2 per cent., calculated as anhydrous calcium sulphate, of the weight of the cement, shall be added.”

In the German Standard Specification, Portland cements are defined as:—

“Products obtained from naturally occurring marls or from artificial mixtures of argillaceous and calcareous substances by calcination to incipient vitrification and subsequent comminution to a state of powder, and which contain at least 1.7 parts by weight of lime to one part by weight of hydraulifactors. For the regulation of technically important properties, foreign substances to the amount of 2 per cent. by weight may be added without altering the designation of the product.”

Gypsum serves to regulate the time of setting, which is retarded by the interaction of its sulphuric acid with the alkalis in the cement. Water acts similarly, and thus many cements show an ignition loss up to 3 per cent., though this includes carbon dioxide as well as water.

In the German definition of Portland cement, only the lower limit of the proportion of lime to hydraulifactors (*i.e.* of the hydraulic modulus) is laid down. The upper limit is usually about 2.2 for artificial Portland cements; for natural Portland cement it may reach 2.4. According to the Russian Standards, the hydraulic modulus is calculated according to the formula:—

$$\frac{\text{CaO} + \text{K}_2\text{O} + \text{Na}_2\text{O}}{\text{SiO}_2 + \text{Al}_2\text{O}_3 + \text{Fe}_2\text{O}_3} = 1.7 \text{ to } 2.2 \text{ or } 2.4.$$

As regards the properties which a cement may exhibit within the limits of the hydraulic modulus, details have been given under "Clay," p. 691. Certain properties, such as time of setting and to some extent also permanency of volume, can thus be deduced from a chemical analysis.

*Clinker.* In a more exhaustive examination of Portland cement, it is often desirable to take into consideration not only the cement itself, but also the clinker from which it was derived.

The mere appearance of the clinker affords some data for the valuation of the cement. Clinker should have a greenish-black colour; if it is chocolate-brown, either incomplete clinkering is indicated, or an addition of fluor-spar before burning, with the object of facilitating clinkering and ensuring stability of the clinker. In the latter case the structure of the clinker is quite dense. A light yellow colour proves that the limestone has scarcely advanced beyond disengagement of its carbon dioxide. Such products are said to be under-burnt; both in colour and in general properties they very much resemble Roman cement, and generally set very rapidly. In contrast to well-burnt clinker they do not stand sprinkling with water, but fall to a wholly worthless powder; this indicates that the lime has not entered into reaction with the hydraulifactors. Well-burnt clinker should show as little tendency to dusting as possible; a decided tendency to dusting points to faulty (usually excessive) calcination, and also to incorrect chemical composition of the slurry. Over-burnt clinker is of dense, basalt-like structure and frequently vitreous in appearance. Such clinker is of little value; when this stage has been passed, however, and complete fusion has been brought about, a cement is obtained which, as Michaëlis has shown, is of excellent quality.

Normally the process of burning is so conducted that the calcium carbonate first gives off its carbon dioxide at  $700^{\circ}$  to  $900^{\circ}$ , and then the calcium oxide reacts upon the clay in much the same way as fused alkalis.

*Ash and Slurry.* During and in consequence of the calcination, cement is always more or less mixed with, and modified by, cinders and ash from the fuel. If for a normal calcination, about 18 parts of fuel are used for every 100 parts of clinker, and there is only 10 to 12 per cent. of ash in the former, there will be as much as 2 per cent. of ash in the finished cement. In an accurate examination, therefore, of the composition of the substances used in the manufacture of a given cement, it is advisable to take the ground and mixed raw materials (*i.e.* the slurry) as basis. In the actual manufacture it is also customary to control the composition of the slurry by rough analytical checks; calcium carbonate is estimated by the calcimeter, as in the case of limestones, and clay by determining the insoluble matter. The content

of calcium carbonate varies between 74.5 per cent. and 76.5 per cent., to which 1 per cent. is generally to be added for magnesium carbonate; the insoluble silicates therefore amount to from 20 to 22 per cent.

*Finished Cement* is a more or less dark grey powder, slightly tinged with green. Lighter or darker shades of colour are produced according to the relative proportions of silicate and ferric oxide present. Thus cements in which the clay is replaced by blast-furnace slag are usually very light grey, with a tinge of blue, due to manganese compounds. Brown discolorations in ordinary Portland cement indicate either an addition of fluor-spar to the slurry, or else faulty burning due to a reducing fire. Powdered Portland cement, in contradistinction to Roman cement, always feels gritty.

#### EXAMINATION OF THE PHYSICAL PROPERTIES OF PORTLAND CEMENT

**Specific Gravity.**—The specific gravity of freshly burnt or re-ignited cement is not less than 3.0 and in most cases lies between 3.1 and 3.2. According to the British Standard Specification,<sup>1</sup> “the specific gravity of

cement when freshly burnt and ground, shall be not less than 3.15; or 3.10 when it can be proved to the satisfaction of the engineer (or purchaser) that the cement has been ground for four weeks.”

The specific gravity can be determined in the usual way by means of the pycnometer. For technical purposes, however, certain special instruments, of which the following are the most important, have come into general use.

*Schumann's Volumemeter* (Fig. 155).

This consists of a glass vessel with a narrow mouth, into which a glass tube graduated from 0 to 40 c.c. is accurately ground. To make a determination, the graduated tube is slightly greased at the lower end, firmly inserted into the neck of the vessel and the apparatus

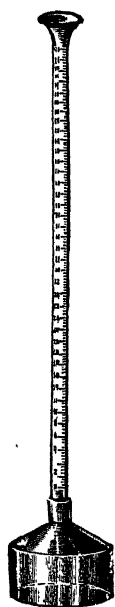


FIG. 155.

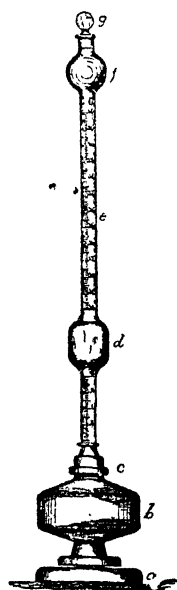


FIG. 156.

filled with petroleum spirit to the zero mark, or a little over. One hundred g. of cement are then introduced in small portions at a time, choking of the tube being prevented by cautiously tapping the apparatus.

<sup>1</sup> *Loc. cit.*, p. 5.

When all the cement has been added it is allowed to stand for two or three minutes and the increased height of liquid read off. For example, if the two readings are 1.8 c.c. and 33.4 c.c. respectively, 100 g. of cement will have displaced  $33.4 - 1.8 = 31.6$  c.c.; hence the specific gravity is 3.16.

In order to avoid the choking of the measuring tube, Suchier has modified Schumann's apparatus by inserting a bulb, *d*, in the tube (Fig. 156); a stoppered bulb, *f*, is also added at the top of the tube, so that adherent particles of cement can be washed down with the liquid. The whole apparatus is shorter and more compact than that of Schumann.

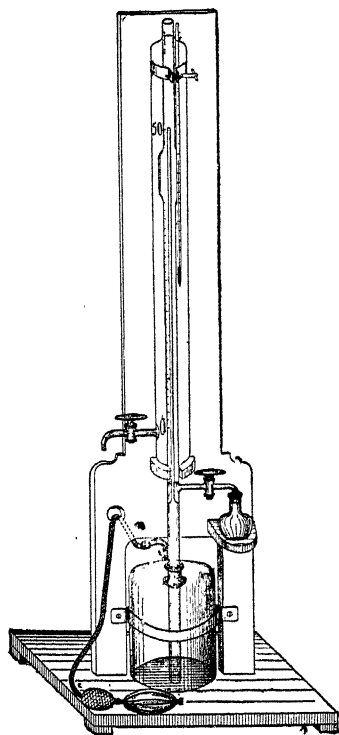


FIG. 157.

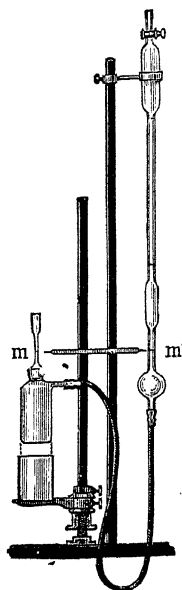


FIG. 158.

P. Beck has proposed the use of carbon tetrachloride in place of petroleum spirit; Schoch does not regard this suggestion as an improvement.

The apparatus devised by Erdmenger and Mann (Fig. 157) is very convenient. It consists of a Woulff's bottle, of which the one tubulure carries a measuring tube of 50 c.c. capacity and the other is connected with a rubber hand-pump. The lower 20 c.c. of the measuring tube are divided into  $\frac{1}{20}$  c.c., whilst the upper 30 c.c. are contained in an ungraduated bulb. The tube is fixed to a stand and is surrounded by a water-jacket provided with an exit-tap; it extends to near the bottom

of the Woulff's bottle and has a narrow tube inside, of which the upper open end coincides with the 50 c.c. mark; the lower end of the measuring tube is closed by a stopcock. By this device the apparatus is always ready for use. The liquid employed for the test is pumped, by means of the rubber ball, from the bottle up the inner tube and so into the measuring tube; the excess drains off through the former and leaves the level at 50 c.c. in the latter; a known volume of liquid can then be drawn off through the stopcock.

In making a determination, 50 g. of cement are weighed into a flask marked to contain 50 c.c., and so much liquid introduced from the automatic burette as is necessary to fill the flask to the 50 c.c. mark. The volume of liquid remaining behind is then read off, and the specific gravity calculated as with Schumann's apparatus.

The instruments described above may be used with other material than cement; that devised by F. M. Meyer is applicable only to Portland cement. This (Fig. 158) consists of a thick-walled barometer, tube graduated from 9.0 c.c. to 10.0 c.c., which is provided with a stopcock at the top and with a zero mark,  $m'$ , at the bottom. The tube is connected by rubber tubing with a filter flask, into the neck of which a funnel tube having a mark  $m$  is accurately ground.

About 110 c.c. of alcohol (methylated spirit which is kept over Portland cement) are poured into the measuring tube from the top, the marks  $m$  and  $m'$  brought to the same level by raising or lowering the filter flask, and more alcohol carefully introduced until the level stands at  $mm'$ . The flask is then raised so as to bring the alcohol nearly up to the stopcock, again lowered, and the level of the liquid carefully readjusted.

To determine a specific gravity, the outer edge of the filter flask is wiped dry with filter paper, the flask raised until the alcohol stands nearly under the stopcock, and the stopcock closed. The stopper of the flask is then taken out, 30 g. of cement introduced and shaken up, the stopper inserted, the stopcock of the barometer tube opened, and the level of the alcohol adjusted to  $m$ . After three minutes the level is readjusted and the volume of the cement read off on the barometer tube. From this volume the specific gravity is calculated by the formula:—

$$s = \frac{W}{V}$$

or it may be obtained by reference to table on page 701.

Schoch is of opinion, as the result of over a hundred comparative determinations, that the Schumann volumeter gives as good results as the others; it is simple in manipulation, and has the additional advantage that a larger quantity of substance can be used for the test.

In addition to the determination of the true specific gravity, the

determination of the bushel-weight, either loose or shaken down, is still in use, especially in France. This test is quite fallacious. Products which are finely ground, and therefore better prepared, will always show a smaller bushel-weight than coarse samples; also, the deduction, for instance, of hectolitre-weight from litre-weight is wrong, because in a larger vessel the cement packs itself more closely, and so gives a relatively higher weight.

### Specific Gravity of Cement.

Weight of substance taken = 30 g. ; volume of alcohol displaced given in c.c.

c.c.	Sp. Gr.	c.c.	Sp. Gr.	c.c.	Sp. Gr.	c.c.	Sp. Gr.
9.00	3.333	9.30	3.226	9.60	3.125	9.90	3.030
1	3.330	1	3.222	1	3.122	1	3.027
2	3.326	2	3.219	2	3.119	2	3.024
3	3.322	3	3.215	3	3.115	3	3.021
4	3.319	4	3.212	4	3.112	4	3.018
5	3.315	5	3.209	5	3.109	5	3.015
6	3.311	6	3.205	6	3.106	6	3.012
7	3.308	7	3.202	7	3.102	7	3.009
8	3.304	8	3.199	8	3.099	8	3.006
9	3.300	9	3.195	9	3.096	9	3.003
9.10	3.297	9.40	3.191	9.70	3.093	10.00	3.000
1	3.293	1	3.188	1	3.090	1	2.997
2	3.289	2	3.185	2	3.086	2	2.994
3	3.286	3	3.181	3	3.083	3	2.991
4	3.282	4	3.178	4	3.080	4	2.988
5	3.279	5	3.175	5	3.077	5	2.985
6	3.275	6	3.171	6	3.074	6	2.982
7	3.272	7	3.168	7	3.071	7	2.979
8	3.268	8	3.165	8	3.068	8	2.976
9	3.264	9	3.161	9	3.064	9	2.973
9.20	3.261	9.50	3.158	9.80	3.061		
1	3.257	1	3.155	1	3.058		
2	3.254	2	3.151	2	3.055		
3	3.250	3	3.148	3	3.052		
4	3.247	4	3.145	4	3.049		
5	3.243	5	3.141	5	3.046		
6	3.240	6	3.138	6	3.043		
7	3.236	7	3.135	7	3.040		
8	3.233	8	3.132	8	3.036		
9	3.229	9	3.128	9	3.033		

**Degree of Fineness of Cement and Sand.**—As stated above, the degree of fineness of cement, both in the finished state, and especially in the condition of slurry, is of the highest importance. The more finely the raw materials are ground, the more intimately will they be mixed and the more complete will be the mutual reaction of the particles during burning. Fine grinding of the raw materials is indispensable when they contain quartz sand. Similarly, the finer the particles of the finished cement are, the more intimately will they enter into contact with each other and with the sand. It is to be borne in mind that lightly

burnt clinker is more easily ground than hard burnt clinker, but that the latter yields the better cement.

The usual method of testing the fineness of the raw mixture or of the finished cement is by means of a series of sieves of definite mesh per unit area.

In Great Britain there is no obligatory standard for Portland cement, but the tests agreed upon by the Engineering Standards Committee for

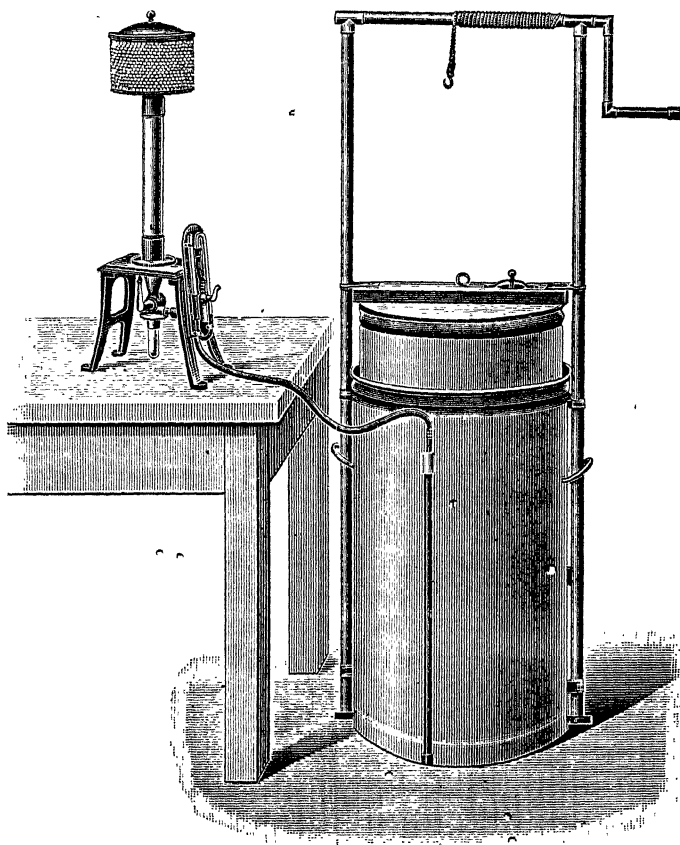


FIG. 159.

the British Standard Specification<sup>1</sup> are now generally known as "Standard."

The sieves specified under this test contain 5776 and 32,400 meshes per sq. in. respectively. The wire of which the coarser sieve is made is 0.0044 inch, and that of the finer sieve 0.002 inch in diameter. The quantity of cement used for a determination is 100 g. After sifting continuously for fifteen minutes, "the residue upon the 5776-mesh sieve

<sup>1</sup> *Loc. cit.*, p. 5.

should not exceed 3 per cent., and that upon the 32,400-mesh sieve should not exceed 18 per cent."

Raw materials should be ground sufficiently finely to completely pass a sieve with 5807 meshes per sq. in., and the residue upon a 31,611-mesh sieve should not exceed 15 per cent.

In Germany sieves are used containing 4900, 2500, and 900 meshes per sq. cm., equivalent to 31,611, 16,118, and 5807 meshes per sq. in. respectively. Average slurry should be so finely ground that it passes the 900-mesh sieve completely and leaves not more than 15 per cent. of residue on the 4900-mesh sieve; for cement, 1 to 2 per cent. may be allowed on the 900 and 20 per cent. on the 4900-mesh sieve.

When materials have been ground by friction or attrition, the use of sieves for separating particles of different sizes gives good results. Where, however, reduction takes place wholly or partially by impact, as in ball mills or mortars, flakes are formed which may be composed of extremely fine particles, but which will not pass through the sieve. In such cases it may be necessary to break up the flakes in order to get a correct estimate of the quantity of fine particles. This source of error is somewhat diminished by effecting the separation by means of a current of air. A convenient form of apparatus based on this principle is the Griffin-Goreham *Flourometer*, the general arrangement of which is shown in Figs. 159 and 160. The supply of air as well as the pressure is regulated by a small gas-holder which contains sufficient air for one test; the pressure of the air supply is indicated by a small pressure-gauge. The duration of the test is about ten minutes. The air supply passes from the gas-holder to the bottom of the conical receptacle F, Fig. 160, into which 10 g. of the cement to be tested have previously been placed. The finer particles of cement, the so-called "flour," are carried away up the tube T, while the coarser grains fall into the receptacle R on the cessation of the air pressure, and are then weighed. Should the test be carried out in the open, the tube T communicates direct with the atmosphere into which the dust escapes, but if the test is made in the laboratory a covered cap is used. This consists of two concentric cylinders of perforated zinc between which cotton wadding, W, is loosely packed. The dust filter should be cleaned from time to time so as to prevent any diminution of the force of the air current. The apparatus can be standardised either by means of sieves or by an actual microscopic measurement of the coarser particles.

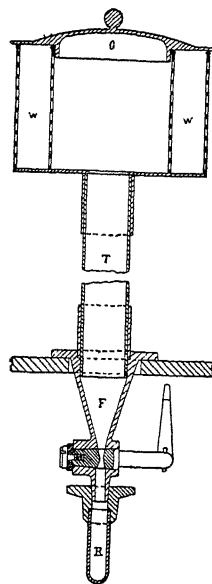


FIG. 160.



The *Sand* used for testing purposes should be of uniform size of grain, although in practice sands consisting of grains of various sizes give a denser mortar and require less cement. In order that the results obtained may be uniform, it is advisable to use sand from the same source for all tests. In England, Leighton-Buzzard sand is in general use. It is washed, dried, and sifted through two sieves of 400 and 600 meshes per sq. in., made of wires 0.0164 inch and 0.0108 inch in diameter respectively. Only that sand which remains between these two sieves is used for testing purposes.<sup>1</sup>

**Hydraulicity.**—The most important test for Portland cement is that for hydraulicity, *i.e.* its power of resisting the action of water to which it may be exposed. The first operation in carrying out this test consists in mixing the cement with sufficient water to produce a paste. This mixing or “gauging” must be done thoroughly, so that the paste produced is as homogeneous as possible. The water used should be fresh and free from muddy particles. The proportion of water required varies with different samples of cement, but the consistency of the paste should be such that it will slide off the trowel in a compact mass and can be moulded to a ball in the hands. A rough test of hydraulicity may be carried out by making a cake or pat of the mortar, and after allowing it to set for twenty-four hours, immersing it in water. To make quite sure of the soundness of a cement by this method would, however, require a considerable length of time, as some cements do not crack or “fly” for some months after gauging. The tensile test is therefore employed; by this means a good idea of the quality of the cement may be obtained in about twenty-eight days.

The amount of water required for mixing with any given sample of cement may be roughly determined by moulding mortars containing varying percentages of water into balls and dropping these on to a hard surface from a height of 50 cm.; no appreciable quantity of the material should adhere to the hands during the moulding, and the balls should be merely flattened and show no cracks after having been dropped. More accurate tests are necessary in the laboratory. One of the best methods consists in enclosing the cement paste in a cylindrical box and allowing a piston of 1 sq. cm. diameter, under a weight of 300 g., to sink into it, the extent of the penetration being read off on a scale. The height of the box, and therefore of the paste within it, is 40 mm., and the scale is accordingly divided from 0 to 40, reading upwards. The right proportion of water with which the paste is considered to be at standard consistency is when the piston penetrates to, and remains at, a depth of 5 to 7 mm. Fresh mixtures are made with varying proportions of water until this consistency is attained.

Some rise of temperature may occur during the tempering or gauging

<sup>1</sup> Cf. *British Standard Specification, loc. cit.*, p. 7.

of cement, especially with quick-setting cements, or with those fresh from the kiln. Any rise of temperature above  $12^{\circ}$  should be looked on with suspicion. Cement which has once set should not be re-mixed for testing purposes.

In all setting tests the cement paste in its box, or the pat on its glass plate, must be kept covered by a watch-glass to avoid premature drying. The pats must always be surrounded by an equally moist atmosphere during the test. If this precaution is not observed, a fallacious, *i.e.* too short, time of setting may result, or else the pats may develop cracks due to desiccation, which are often mistaken for cracks due to blowing; the former cracks are generally spiral and do not gape at the surface. They arise from the rapid drying of the surface, with which the interior of the pat cannot keep pace; this brings about internal strains which relieve themselves by the formation of cracks.

Further, the temperature of the air and of the water used in gauging are of considerable influence on the time of setting. High temperatures accelerate it greatly, low temperatures retard it. The temperature should be kept between  $58^{\circ}$  and  $64^{\circ}$  F.<sup>1</sup> ( $14.4^{\circ}$  to  $17.8^{\circ}$  C.).

In the case of extremely rapid-setting cements it may easily happen that setting begins when the cement is first tempered. In these circumstances a second, but less marked, setting is often noted. Cements of unknown properties are therefore first examined by tempering them with a large quantity of water, and watching for the appearance of a crust. Very rapid-setting cements are best allowed to stand in the open, or are toned down with a little water or plaster of Paris, before testing, but frequently the usual direct test is purposely asked for.

Quick-setting cements usually require a greater proportion of water in tempering than normal and slow-setting cements. In general, the admixture of water varies between 25 and 36 per cent., and only rises to 40 per cent. for perfectly fresh cements or exceptionally rapid-setting products. According to the British Standard Specification, "the quantity of water used in gauging shall be appropriate to the quality of the cement and shall be so proportioned that when the cement is gauged it shall form a smooth, easily worked paste, that will leave the trowel cleanly in a compact mass." An excess of water must be avoided; in this case the cement is "drowned" in the same way as quicklime; that is, it is greatly hindered in developing its mechanical properties.

The two most important properties of good cement are soundness and mechanical strength. Cement, whether neat or mixed with sand, must permanently retain the shape into which it has been moulded and has set, without becoming soft, or warping or cracking, or, above all, disintegrating. Moreover, it must attain, in hardening, as great a strength as possible. These two points practically embrace all the

<sup>1</sup> Cf. *British Standard Specification*, p. 6.

requirements of a cement with regard to its fitness as a binding material.

**Time of Setting.**—The time of setting of cements may vary from

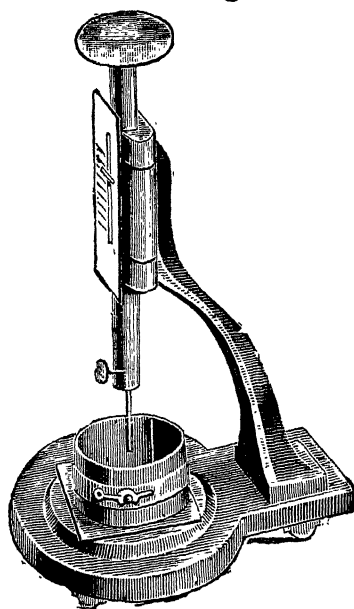


FIG. 161.

five minutes to six or seven hours or more. It is determined by means of a Vicat needle (Fig. 161); the form recommended by the Engineering Standards Committee<sup>1</sup> is shown in Fig. 162. The needle C of the latter has a flat end  $\frac{1}{8}$  in. square, and weighs in all, exclusive of the flat lifting ring,  $2\frac{1}{2}$  lbs. It is applied gently to the surface of the paste, and the cement is considered as finally "set" when the point fails to make an impression; the time of setting is thus determined. When tested in this way, a cement which sets in from ten to thirty minutes is termed "quick"; from half an hour to two hours, "medium"; and from two hours to seven hours

"slow." As temperature has much influence on the rapidity of setting of cements, it is advisable to conduct all tests of this kind at a temperature of from  $58^{\circ}$  to  $64^{\circ}$  F.<sup>2</sup> ( $14.4^{\circ}$  to  $17.8^{\circ}$  C.).

**Tests for Permanency of Volume.**—During the setting, especially at a high temperature, there is usually a slight expansion of the cement, the measurement of which is of great importance. The simplest apparatus for determining the amount of this expansion is that of Le Chatelier, in which the paste is placed in a split metal tube and the extent to which the tube is expanded measured by two indicators.

The form of this apparatus as adopted by the Engineering Standards Committee<sup>3</sup> is shown in Figs. 163 and 164. The split cylinder is made of spring brass or other suitable metal 0.5 mm. (0.0197 in.) in thickness; the dimensions of the mould and the distance of the indicators A A from the centre of the cylinder are given in the figure.

A form of the same apparatus in which the expansion can be read

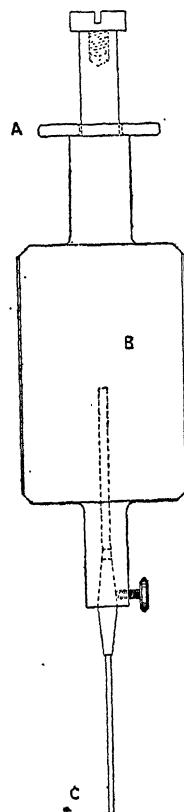


FIG. 162.

<sup>1</sup> *Loc. cit.*, p. 7.

<sup>2</sup> Cf. *British Standard Specification*, p. 7.

<sup>3</sup> *Loc. cit.*, p. 8.

off on a scale fixed to one of the indicators, can also be used for this test.

The method specified for carrying out the test is to place the mould upon a small piece of glass and fill it with the gauged cement, keeping the edges of the mould together during the operation. The mould is then covered with another glass plate upon which a small weight is placed and the whole immersed for twenty-four hours in water at the normal temperature (58° to 64° F.). After measuring the distance between the indicator points, the mould is placed in cold water, which is brought to

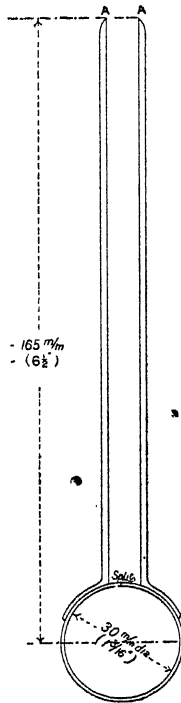


FIG. 163.

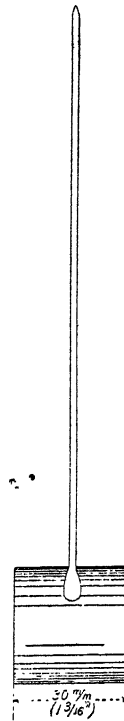


FIG. 164.

the boiling-point in from fifteen to thirty minutes and kept boiling for six hours; after cooling, the distance between the points is again measured. The difference between the two measurements represents the expansion of the cement, which should not exceed 10 mm. in the case of cements that have been aerated for twenty-four hours or 5 mm. with those that have been aerated for seven days.

A more accurate apparatus for testing the amount of expansion is that of Bauschinger<sup>1</sup> (Fig. 165).

This consists of a brass frame, A, to one side of which is attached a

<sup>1</sup> *Mitteilung. a. d. Mechan. tech. Laboratorium der tech. Hochschule, Munich, 8, 13.*

delicate micrometer screw, on the scale B of which hundredths of a revolution can be read off and thousandths estimated; whole revolutions are registered by the scale C. On the other arm of the frame is the fulcrum of a right-angled lever, D D, the short arm of which ends in a blunt steel point, while the longer one bears an indicator which is pushed towards the left by means of a spring, E. This spring is fixed to an upright which also carries the small scale F. The micrometer screw terminates in a blunt steel point. The two steel points fit into

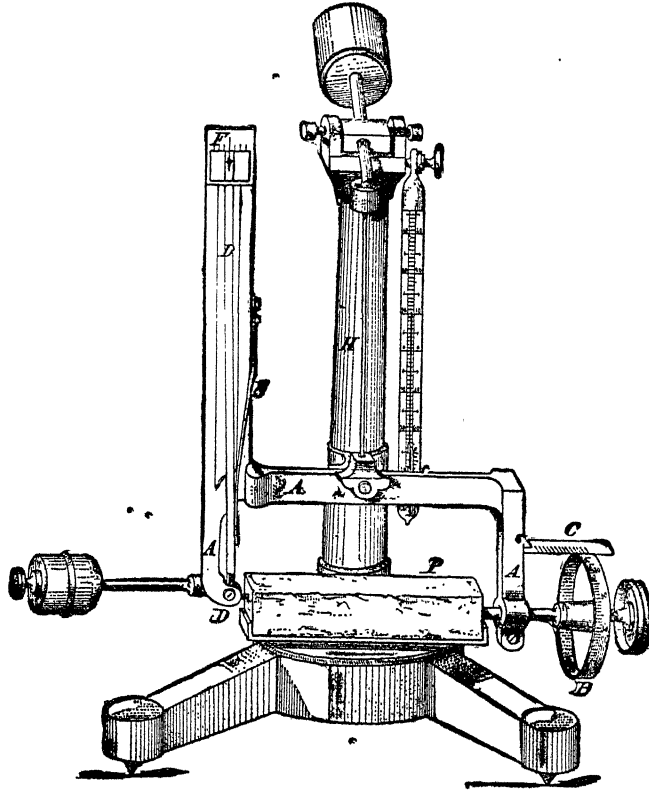


FIG. 165.

depressions in two small cones which are let into the test pieces. In order that these contacts may be made without lateral pressure, the frame A is suspended from the middle of its cross-bar, by means of the brass wire H, to a beam, so that it can move easily either up or down or to either side. This is effected by ball-bearings at each end of the wire H, and the frame itself can rotate on a horizontal axis by means of two pointed screws. The other end of the beam is provided with an adjustable counterweight to balance the weight of the whole frame. The micrometer screw having been applied to the test piece, is moved

forward until the longer arm of the lever points to the centre of the scale. It may then be assumed with certainty that the steel points of the screw and of the indicating lever stand in contact with the test piece under a definite pressure equal to that of the spring E, and the micrometer can then be read off. The adjustment of the indicating lever must always be carried out from one side, *e.g.*, by turning the screw forwards, so as to eliminate the back-lash of the latter.

It is important that the measurements be carried out at, or be reduced to, one and the same temperature; the correction for  $\pm 1^\circ$  is  $\pm .002$  scale divisions. The test pieces should be kept in air or water at the ordinary temperature for at least three hours before measurement.

The test piece is a prism of square section 95 cm. long; twenty-four hours after moulding, it is fitted with the contact cones, and the first measurement is made forty-eight hours after moulding. Care must be taken, in consecutive measurements, to insert the test pieces with uniform precision and always in the same position.

The zero point of the micrometer scale corresponds to a gap of 95.000 mm.; each turn of the screw is equal to one scale division = 0.500 mm., and each drum division =  $\frac{0.500}{100} = .005$  mm.

If the length of a test piece were 100.000 mm., 10.000 scale divisions would accordingly be read off, whence the length would be calculated as  $10 \times 0.500 + 95.000 = 100.000$  mm. A standard 100.000 mm. measure, consisting of a steel rod mounted in wood, is supplied for purposes of control.

**Accelerated Tests for Permanency of Volume.**—Of the many more rapid or accelerated tests for permanency of volume, each of which has advantages in special cases, the following may be mentioned:—

*Heintzel's Calcining Test.* About 150 g. of cement are mixed with sufficient water to produce a paste that can be rolled into a ball in the hands. In most cases about  $\frac{2}{3}$  to  $\frac{3}{4}$  of the amount of water necessary to produce a paste of standard consistency will suffice. The ball thus produced is placed immediately upon either a piece of wire gauze or an iron plate and heated for three hours with an ordinary Bunsen burner. Unsound cement will flake off and crack more or less on the under side of the ball. The chief advantage of this test is that it will show, in a very short time, whether a cement is sound, but it would not be safe to assume that a cement which does not pass so severe a test is necessarily unsound.

*Roasting Test.* A paste is made with 75 g. of cement and sufficient water to produce the normal consistency, and moulded into a sphere by means of a round spoon. The ball is placed upon a thin piece of glass, which is jarred until a cake is formed about 10 cm. in diameter and 1 cm. thick. The edges of the cake should not be too thin. The cakes

thus prepared should be kept in moist air until set, or for twenty-four hours. They are then immersed in water until saturated, and placed upon an iron plate, where they are heated for three hours at a temperature of  $180^{\circ}$  to  $210^{\circ}$ . This test may be modified by covering the cake with a watch-glass at the commencement of heating, so that it is surrounded by steam at the beginning of the test.

*Boiling Test.* This test, which is usually associated with the name of Michaëlis, is carried out with pats or cakes made as in the preceding test. These are placed in a vessel full of cold water, and covered with a watch-glass; the water is then heated to boiling for three hours. Under this treatment unsound cement will crack or even fall to pieces.

The causes of "flying" or "blowing" are very varied, and include too coarse grinding, defective mixing of the raw materials, imperfect burning, too high a percentage of sulphates, or too much lime. Magnesia, when present in quantities greater than 5 per cent., is said to cause "flying," but the proof of this has not yet been conclusively established.

*Tetmajer's investigations on the tests for Permanency of Volume.* The numerous experiments of Tetmajer<sup>1</sup> on permanency of volume have established the following points with regard to the soundness of cements:—

1. Portland cements which stand the ordinary pat tests well, both in air and in water, show equally good behaviour under accelerated tests.
2. Portland cements which, in the air test, crumble, develop cracks, or fall to powder, invariably fail in the accelerated tests.
3. Portland cements which disintegrate after about three hours in the boiling test, or warp, crack, or lose coherence in the roasting test, or develop the characteristic fissures in the calcining test, break down on exposure to air, frequently after not more than six months.
4. Portland cements which fail in the boiling and roasting tests do not stand either exposure to air or to water. With these cements the first signs of unsoundness often make their appearance after very few days, and decay sets in rather more rapidly under water than in air.
5. Faultless behaviour under water by no means implies the same in air. There are some Portland cements which keep well under water but begin to disintegrate gradually in air, though perhaps only after a long time.

**Increase of Volume on mixing with Sand.**—The increase of volume of sand-cement mixtures is determined with the same apparatus as is employed in testing the increase of volume in slaking lime (*cf.* Fig. 151, p. 670), and the test is similarly carried out except that the heating on the water-bath is dispensed with. One hundred g. of the cement are mixed with the various proportions of sand, *i.e.*,

<sup>1</sup> *Hydraulische Bindemittel*, 1893, pp. 230-231.

300, 400, 500, etc., g., the mixture charged into the box, and water added little by little, with continual tapping, until a paste is formed which leaves a few c.c. of water on the surface. The water is then cautiously removed by means of absorbent paper, and the vessel covered with a watch-glass, and left for twenty-four hours. Then 200 c.c. of water are added from a pipette and the volume of the cement paste read off directly.

**Permeability to Water.**—This property is determined by means of the apparatus shown in Fig. 166.<sup>1</sup> It consists of a reservoir in the shape of a short bent tube with a cast-iron cap, which carries a graduated glass tube divided into c.c. The test piece, protected by two rubber washers, of  $4\frac{1}{2}$  cm. internal diameter, is clamped between the reservoir and the cap. The reservoir is provided with a manometer and ends in a flange, by means of which it is connected with a water supply having a head of at least  $4\frac{1}{2}$  atmospheres pressure. The apparatus is solidly mounted on a concrete bed. A T-piece with a stopcock is interposed between the reservoir and the water supply for the purpose of emptying the apparatus and of regulating the pressure of the water. During the test this stopcock is half opened, and thus allows part of the water to run off; by this means a fairly uniform pressure is maintained. The test pieces are gauged by hand. The cement is mixed with a definite proportion of sand and patted into a brass ring of 7.2 cm. internal diameter and 2.0 cm. height; after twenty-four hours the test pieces are laid under water.

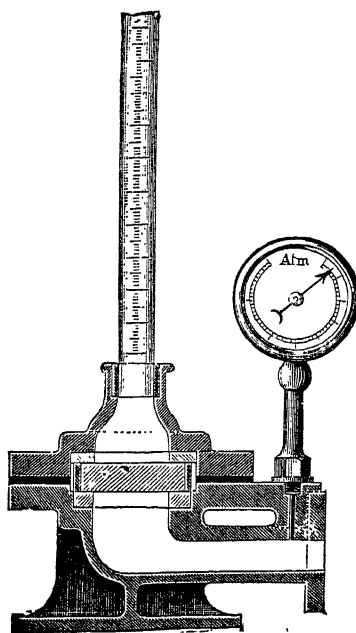


FIG. 166.

To carry out the test, the discs of cement are saturated with water under the receiver of an air-pump and then inserted, together with the brass moulds, into the apparatus, which has been previously charged with water. The upper part of the apparatus is filled with water from a pipette or rubber tube up to any desired mark on the measuring tube, the reading taken, and the water turned on. After 1, 2, 4, 8, 24, etc., hours, readings are again taken, and the results expressed in terms of unit time and unit water pressure.

If a water supply of adequate head is not available, the small

<sup>1</sup> Cf. Tetmajer, *Hydraulische Bindemittel*, 1893, pp. 109-11.



apparatus devised by Michaëlis, which gives fairly satisfactory results, may be employed (Fig. 167). In this apparatus the vacuum is obtained either by mercury or by an air-pump. It consists of a glass cylinder, A, provided with two tubulures and a ground flange on which the test piece M is fixed; the cap B supports a graduated measuring tube, D, which is attached by means of a rubber stopper. This tube is graduated

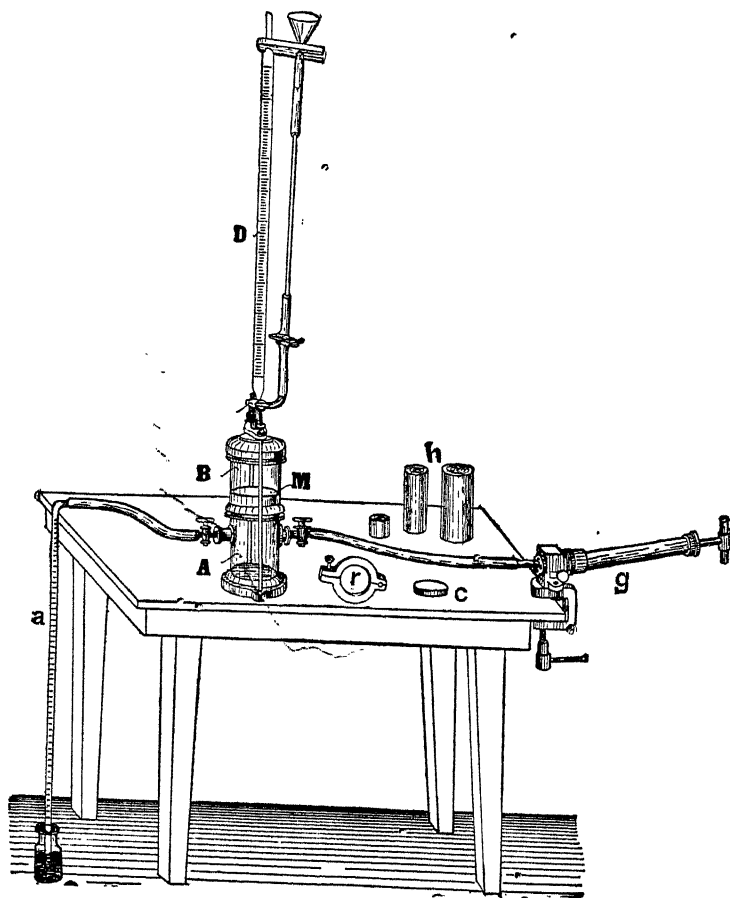


FIG. 167.

for 200 c.c. in divisions of  $\frac{1}{2}$  c.c. and communicates laterally with a funnel, through which it is filled.

The tubulures of the lower vessel A are connected on one side with an air-pump, g, and on the other side with a small mercury gauge, a.

In making a test, a round test piece, c, 10 mm. thick and tapering slightly downwards, is placed in the carrier and made tight with a rubber washer of 20 sq. cm. sectional area. The remaining portions of the apparatus are then placed in position, the measuring tube

filled with water and adjusted to zero, and the funnel tube closed by a clip.

The lower glass vessel is then evacuated by means of the air-pump. Under the pressure of the atmosphere the water is thus forced through the test piece, and the amount which has penetrated can be read off at intervals from the measuring tube and calculated per 1 sq. cm.

The Amsler-Laffon apparatus (Fig. 168) is also independent of a water supply. It consists of an accumulator charged with compressed air, which drives water from below through the test piece; the latter is fixed at the top of the accumulator and the water which passes through collects in a glass tube graduated in c.c. The pressure within the accumulator is indicated by a manometer. The accumulator is filled with air and water, with the aid of a hand-pump; a continuous and uniform pressure upon the test piece is thus secured. No replenishment of the compressed air is required, except when higher pressures are desired, as there is no leakage of the contained air. The effective area of the test pieces, through which alone water can escape, is a circle of 5 cm. diameter; they may be 2, 3, or 4 cm. thick.

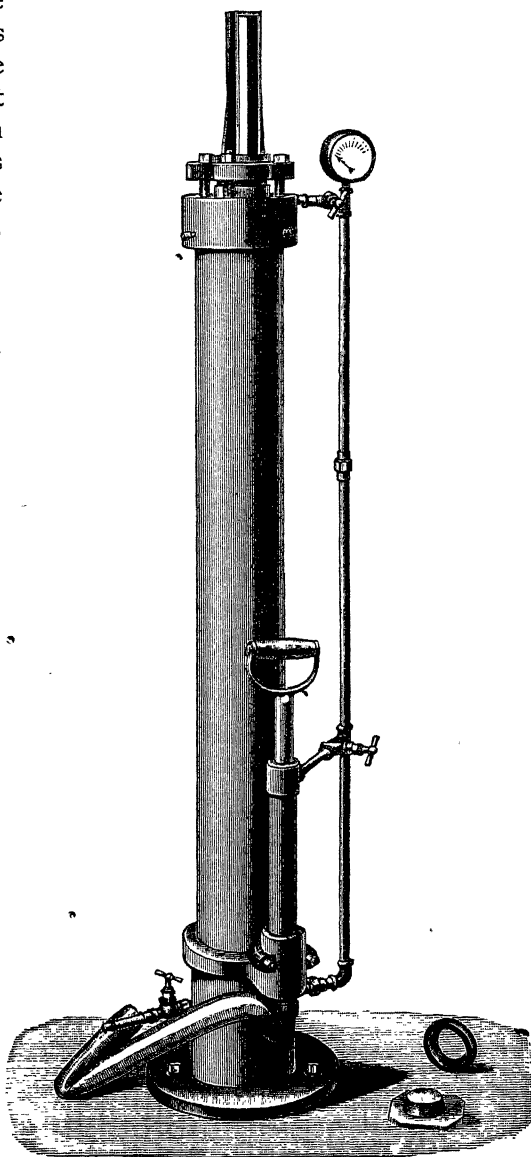


FIG. 168.

**Resistance to Frost.**—For this test a refrigerator of the Linde

type is used, giving temperatures down to  $-30^{\circ}$ ; any other good form of refrigerator can be employed.

Cubes of 7 cm. length are used as the test pieces, which are saturated with water in vacuo and allowed to remain for twelve hours under water; they are then placed for four hours in the refrigerator, preferably enclosed in tightly fitting zinc covers. They are then dipped again in water to make up for superficial evaporation and again kept at about  $-20^{\circ}$  for four hours. The test pieces are then thawed overnight, in water at the ordinary temperature, and on the following day again frozen, twice successively, for periods of four hours. This alternate freezing and thawing is repeated twenty times. Finally the test pieces thus treated are subjected to the crushing tests, and the results compared with those obtained with unfrozen specimens of the same material.

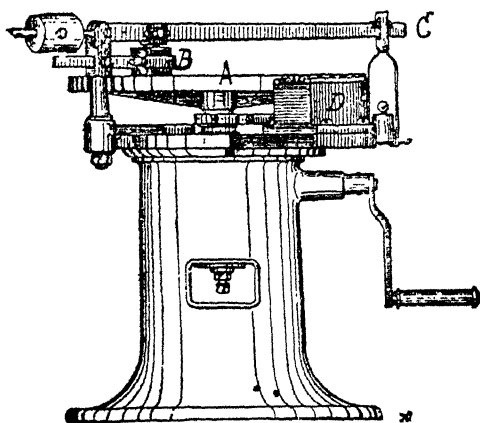


FIG. 169.

pieces B. By means of two weighted levers, C, pressures up to 30 kilos can be placed upon the test pieces, which are ground down with Naxos emery on a track of 50 cm. radius. The number of revolutions (200) is automatically controlled. The test pieces are weighed to within a decigram before and after treatment. The loss of weight represents the degree of abrasion; this is fairly large at the outset, but decreases considerably in the course of time.

**Abrasion Test.**—To determine the resistance of a cement to abrasion, the rotating disc apparatus devised by Bauschinger (Fig. 169) is employed. The disc A, which is 3 cm. thick and 122 cm. in diameter, is trued to a plane surface, and revolves upon a vertical spindle. The upper bearing of this spindle carries two radially movable arms, reaching about 3 mm. above the disc, which serve to hold the test

#### MECHANICAL TESTS FOR PORTLAND CEMENT

The utility of Portland cement is mainly due to the very considerable hardening which it undergoes after the initial setting, either neat or with admixtures. The strength attained by Portland cement in consequence of this hardening, which is particularly vigorous in the earlier stages, places it far above all other binding materials. This is in accord with the rule that the strength of such a material increases

with its density ; a dense material yields a dense, and therefore strong, product.

Thus the strength of a Portland cement is largely conditioned by the degree of condensation brought about in burning. This is gauged by determining the specific gravity. But the hardening properties, and consequently the strength, of a cement also depend on other factors, among which the chemical composition is of special importance. The higher the percentage of lime within the admissible limits, the greater is the initial hardening, whereas a highly siliceous cement, though weaker at the outset, attains a greater ultimate strength. Cements containing much iron show inferior mechanical strength ; calcium ferrate is attacked by water, whilst calcium silicates and aluminates, especially the mono-compounds, are very resistant towards water.

The water used in tempering is not without influence, inasmuch as hard and carbonated waters produce greater strengths, soft waters lesser strengths. Sea-water, owing to its content of sulphuric acid as magnesium sulphate, has a decomposing effect.

The time of setting, again, is a determinant factor, since quick setting favours low strengths, and slow setting, high strengths. The fineness of the cement also plays a part, provided the original clinker was fully burnt.

Further, the nature of the sand mixed with the cement influences the strength ; clear sand, free from clay, having sharp edges and corners, and of mixed grades of fineness, is the most favourable.

Owing to the powerful condensing effect of the burning process, the neat strength of cement is so high as to differentiate it from other binding materials. Neat tests are accordingly often made merely with the object of identifying a cement as Portland cement. The crushing strain more especially adapts itself to this purpose.

The following mechanical tests are applied to Portland cement :—

1. The tensile strain.
2. The crushing strain.
3. The adhesion.
4. The bending strain.

**The Preparation of the Test Pieces.**—To prepare the test pieces, neat cement or the sand mixture is thoroughly incorporated with the required quantity of water. Test pieces of unmixed cement usually require from 19 to 22 per cent. of water for tempering, whilst the sand test requires from  $7\frac{1}{2}$  to 11 per cent. ; in this case also quick-setting cements need more water than slow-setting cements, and hand-gauged briquettes more than machine-gauged ones. Care must be taken, on the one hand, not to allow the initial setting to supervene, and, on the other hand, not to crush any grains of sand with the trowel. The best instrument to use for the mixing is a fork with short, thick prongs.

Where large numbers of briquettes have to be made, some form of

mixing machine is useful; that of Steinbrück-Schmelzer (Figs. 170 and 171) is much used on the Continent for this purpose. It consists of an annular trough, *s*, in which a roller, *w*, runs, and which revolves at a

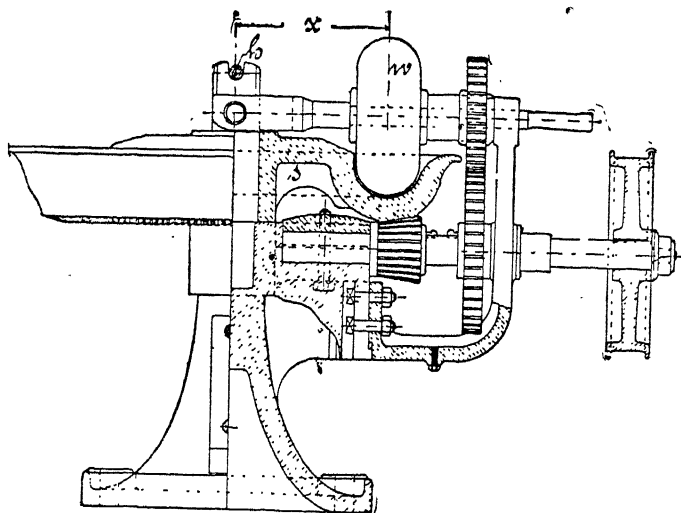


FIG. 170.

different rate from the mixing pan itself, but in the same direction. The paste is thus squeezed and spread out by the roller, after which it is loosened and turned over by the scrapers *m* and *n* (Fig. 171). A third

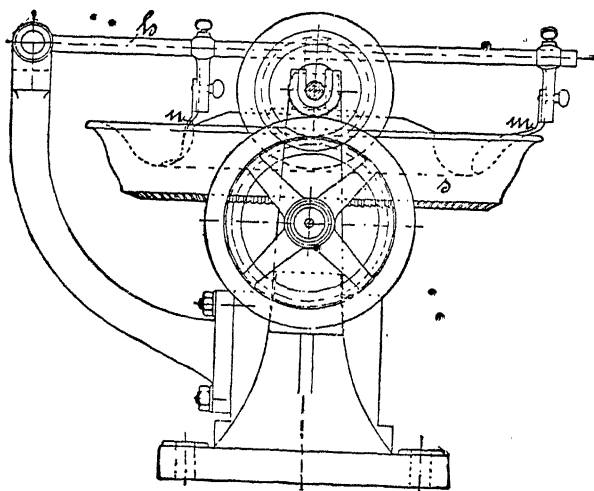


FIG. 171.

scraper, not represented in the figures, is provided to keep the roller clean. The machine is driven either by a hand crank or by power. When running at full speed the pan is intended to make eight revolu-

tions per minute; it takes a charge of 500 g. of cement, plus 1500 g. of sand, which serves to make eleven or twelve test pieces.

The paste, when homogeneous, is filled into the moulds and beaten down by hand or by machinery until it has become quite compact. This point is reached, in hand moulding, when the paste has assumed a plastic consistency and a little water has collected on the upper surface. In machine moulding, similarly, the separation of water occurs after a certain number of strokes.

For gauging cement, etc., by hand, a spatula about 350 mm. long with a beating surface of 40 × 80 mm. and weighing 250, 300, or 350 g., was formerly used, but a heavier tool up to 750 g. in weight is now preferred.

The form of briquette recommended by the Engineering Standards Committee<sup>1</sup> is shown in Fig. 172, upon which the dimensions are given in inches.

When a number of briquettes have to be made, the moulds may, with advantage, be arranged in series and fixed in some simple manner such as that shown in Fig. 173.

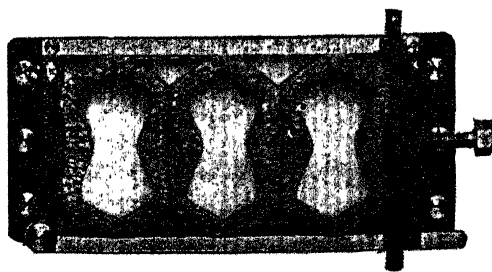


FIG. 173.

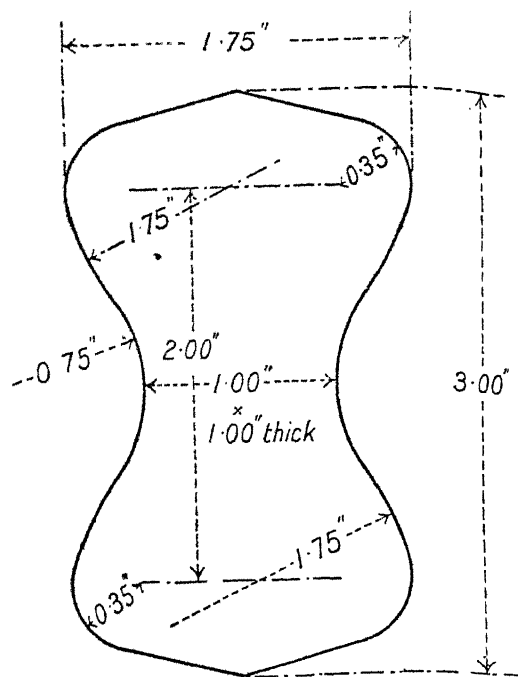


FIG. 172.

Single moulds are usually made in halves, which are held together either by screws or by a spring clip sliding into grooves cut in the sides of the mould. In either case precautions must be taken to prevent the opening of the mould during filling.

According to the specification of the Engineering Standards Committee the moulds are filled by hand and without mechanical ramming, an iron plate being used as a foundation. When the cement has set

<sup>1</sup> *British Standard Specification*, p. 6.

sufficiently to enable the mould to be removed without injury to the briquette, the latter is placed in a damp atmosphere for twenty-four hours after gauging. It is then placed in fresh water at a temperature of from 58° to 64° F. until required for breaking. The water should be renewed every seven days.<sup>1</sup>

The *Sand Test* is carried out by mixing "one part of the cement with three parts by weight of dry standard sand," and gauging with such a proportion of water that "the mixture is thoroughly wetted and that there is no superfluous water when the briquettes are formed." The form of the moulds and the method of filling are the same as for the neat test.<sup>2</sup>

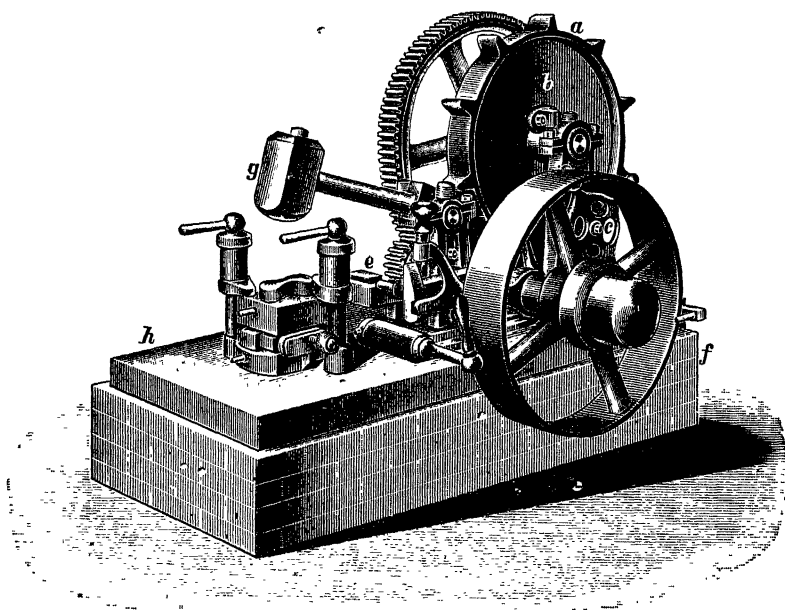


FIG. 174.

For the mechanical moulding of briquettes either Böhme's hammer or Tetmajer's rammer is used.

Böhme's apparatus (Fig. 174) consists of a balanced hammer, *g*, weighing 2 or 3 kilos, which is pivoted at the end of a shaft and is made to fall from a constant height of 25 cm. The hammer is set in motion, through the cogs *a* of the ten-toothed wheel *b*, by the pulley *f*, and makes 120 or 150 strokes a minute. After 12 or 15 revolutions of the wheel *b* a counting device, *c*, automatically puts it out of gear, the bolt *e* is released, and by acting on *f* stops the wheel.

This machine is very widely employed, but is defective in so far as the impact of the hammer is oblique, and its height of fall changes slightly in the course of moulding.

<sup>1</sup> *British Standard Specification*, p. 6.

<sup>2</sup> *Ibid.*, p. 76.

Tetmajer's rammer (Fig. 175) consists of a weight of 2 or 3 kilos, which is lifted by a friction gear and falls from a height of 250 or 300 mm. The number of strokes is 120 or 150, after which the apparatus is automatically stopped. It is adapted for making briquettes for either tensile or crushing tests.

The mechanism is as follows:—The weight or monkey B is lifted by the friction of the wheels D and c. The height of fall is thus invariable and independent of the height of the cement paste under experiment.

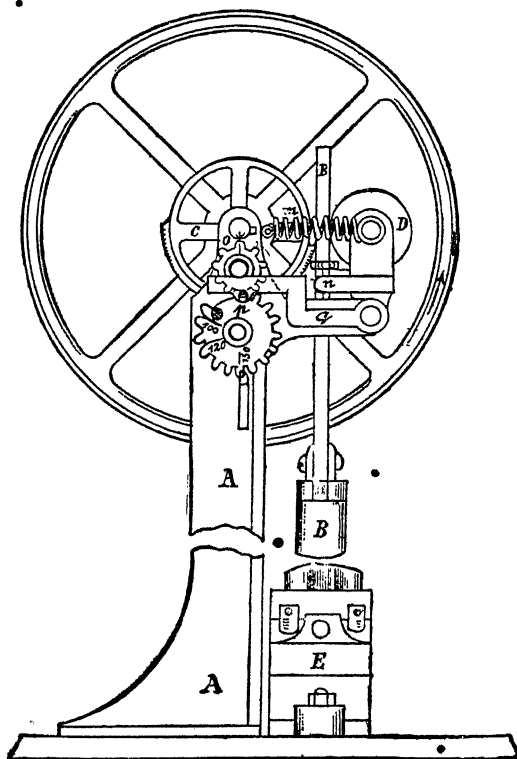


FIG. 175.

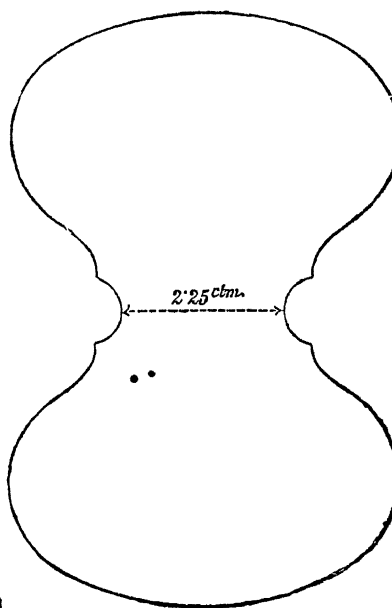


FIG. 176.

Automatic stoppage is brought about by means of the counter *o p*.

The moulds for tensile test briquettes most in use on the Continent are in the shape of a figure 8 (Fig. 176). They are 22.2 mm. high and 22.5 mm. wide at the constriction, which gives a breaking area of 5 sq. cm. For the crushing test hollow cubical moulds of 7.07 cm. edge are used, so that the area operated upon is 50 sq. cm. The cubic capacity of the former is 70 c.c., that of the latter 354 c.c. It follows that, in spite of all precautions, it is impossible to prepare truly equivalent test pieces for the two tests, which therefore cannot be strictly comparable. This is of importance, inasmuch as Böhme's



apparatus makes no pretence of equal treatment. In most works the apparatus is fitted with the 2-kilo hammer and adjusted for 150 strokes only, and is used impartially for tensile and crushing tests. Nevertheless, it is customary to take into account the ratio of tensile to crushing strain in a complete test.

After the cement paste has been filled into the mould, the excess is scraped off with a straight and rigid knife and the upper surface smoothed by a few strokes of the same. The mould is then opened

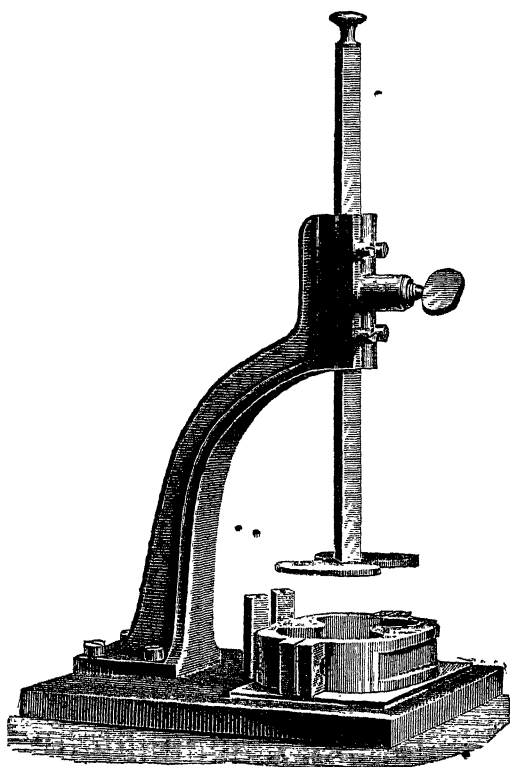


FIG. 177.

and the briquette cautiously removed. In the case of briquettes for the crushing test, this can only be done, owing to the adhesion of the cement, after setting or after, say, twenty-four hours, unless an ejector be used. This course is very much to be recommended, since the resulting test pieces are smoother and firmer, and the mould is then immediately ready for another test. Also, moulds made in one piece can be employed, which secures greater uniformity in the area of the briquette.

Michaëlis<sup>1</sup> has constructed a small and handy apparatus for removing briquettes from their moulds (Fig. 177). A rod of square section having a knob at the top and a steel plate or piston at the bottom fitting into the mould, moves vertically in a massive holder, in which it can be fixed by a set-screw. The base of the apparatus is provided with two quadrangular guide-bars corresponding to two notches in the mould, whereby accurate adjustment of the mould with respect to the steel plate is secured. The mould and its contents are placed in position under the piston, which is let down until it rests on the cement and is then screwed up; the mould can then be slipped upwards from the briquette. When the latter is clear, the piston is slightly raised, and the test-piece removed. The consistency of the test piece is in no way

<sup>1</sup> *Tonindustrie Zeit.*, 1891, 15, 337, 338.

affected by this procedure, and it is possible, moreover, to obtain absolutely parallel upper and lower surfaces, which is an advantage in case the broken briquette is to be subsequently subjected to the crushing test. For this purpose a few light taps are given to the piston when resting on the cement, and should special care be desirable, so many strokes less may be given in the ramming. The apparatus is accordingly serviceable in several respects, both for tensile and crushing tests.

- The released briquette is immediately placed in a zinc box closed by a well-fitting lid, in order to prevent desiccation, by warm draughts of air, the briquette being thus surrounded by an evenly moist atmosphere. After twenty-four hours, or at any rate not before complete setting, it is either exposed to the air or immersed in water.

Air-exposure tests are rarely made; the briquettes dry unevenly,

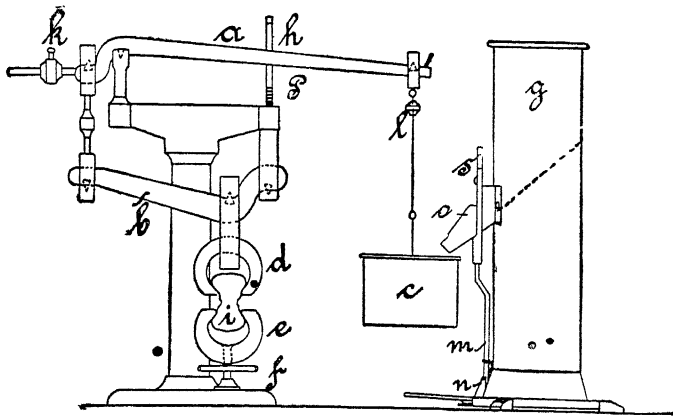


FIG. 178.

whereby internal stresses are set up and low values for mechanical strength result.

Neat tests also are not invariably carried out, although they are useful for distinguishing Portland cement from other cements.

The briquettes are left under water uninterruptedly until the actual testing takes place. They are then wiped dry and fixed in the testing machine.

**The Tensile Strain.**—Of the many forms of apparatus which have been devised for the determination of the tensile strain of cements, that of Michaëlis fulfils all the necessary requirements, and is the most frequently used. There are also several modifications of this apparatus which are made and employed in this country.

This machine, which is shown in Fig. 178, is essentially a system of two levers, *a*, *b*, which have a working ratio of  $1:10 \times 5 = 50$ . The upper clip *d*, for holding the briquette *i*, hangs upon a stirrup; the lower

clip *e* is fastened by a ball-socket to a screw with a finger-wheel, *f*. The contact areas of the clips are rounded so that the force is applied at

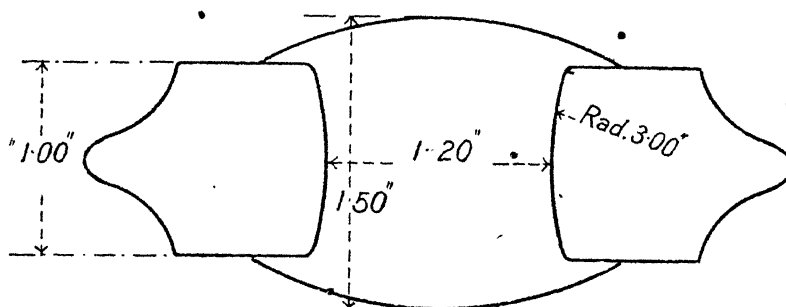


FIG. 179.

four points. A counterpoise, *h*, serves to adjust the whole system to a state of equilibrium, so that the two sets of knife-edges lie in horizontal planes.

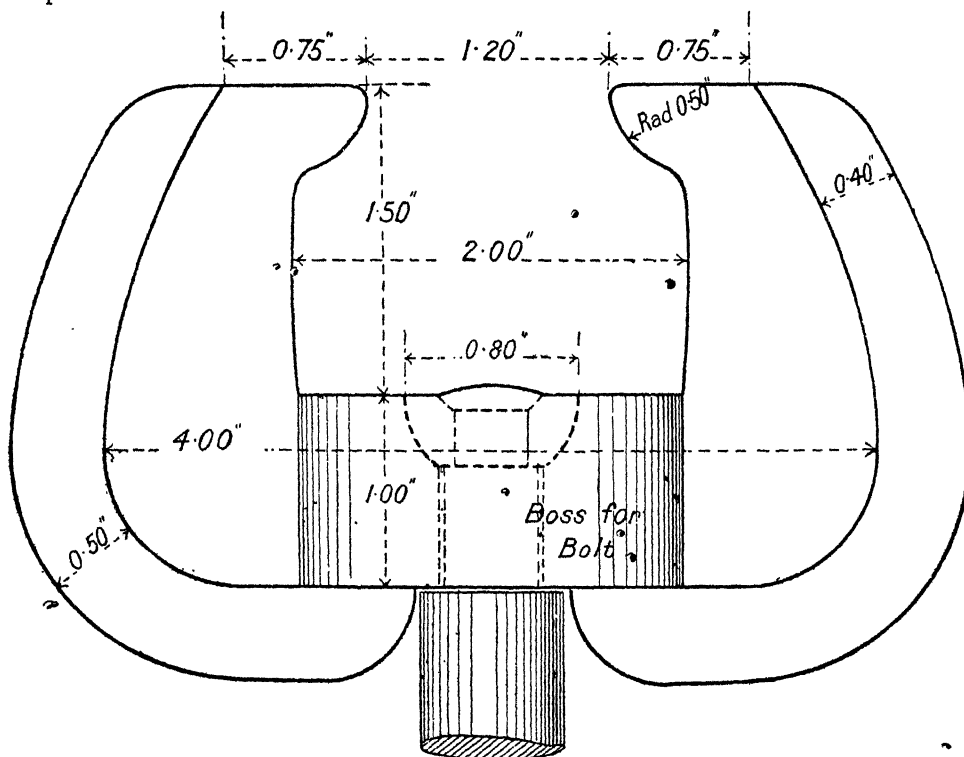


FIG. 180.

In conducting an experiment, the briquette is first loosely hung in the clips and the bucket *c*, which is provided to hold shot, is suspended

from the hook *l*. The bucket should hang about 7 cm. above the ground or bench. By turning the screw *f* the clips are brought firmly up against the briquette; it is important that they should grip it evenly, so that the pressures exerted at the four points of contact shall be equal. Shot is then allowed to run into the bucket, which is supported at the start by the finger in order to lessen the impact of the shot. The running in of the shot is continued until the briquette breaks across the constriction; the bucket then falls down and automatically shuts off the supply of shot. The bucket and its contents are then weighed, and the breaking tensile strain of the briquette calculated per unit area.

The form of the clips between which the briquettes are held while being subjected to the tensile test is of great influence on the results. The clips recommended by the Engineering Standards Committee<sup>1</sup> are shown, in actual size, in plan in Fig. 179 and in elevation in Fig. 180.

The rate of increment of the weight applied is also of importance. It should be "steadily and uniformly applied, starting from zero, increasing at the rate of 100 lbs. in twelve seconds";<sup>2</sup> this rate can be easily regulated by experiment with most of the testing machines in use.

When very weak materials, such as mortar, are to be tested, the bucket is replaced by a much lighter one, the weight of which is eliminated by adjusting the counterpoise *k*. In this way tensile strengths down to 1 kilo can be determined.

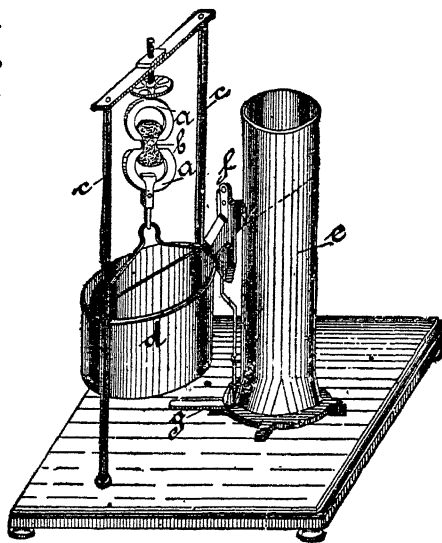


FIG. 181.

A simpler apparatus, in which the multiplying ratio is dispensed with, is shown in Fig. 181. The clips *a a*, which hold the briquette *b*, are suspended from an iron stand, *c c*. The bucket *d* hangs directly upon the lower clip, and the shot-feed is controlled, as above, by the slide *f* and the spring lever *g*.

According to the specification of the Engineering Standards Committee,<sup>3</sup> neat cement is tested after seven and twenty-eight days from gauging. Six briquettes are made and the average tensile strength of the six tests is accepted as that of the cement. Good cement should bear a tensile strain of 400 lbs. on the section of the briquette, square

<sup>1</sup> *British Standard Specification*, p. 6.

<sup>2</sup> *Ibid.*, p. 6.

<sup>3</sup> *Ibid.*, p. 7.

inch, in seven days from gauging and 500 lbs. in twenty-eight days. Also, "The increase from seven to twenty-eight days shall not be less than :—

- 25 % When the seven-day test falls between 400 lbs. to 450 lbs.
- 20 % When the seven-day test falls between 450 lbs. to 500 lbs.
- 15 % When the seven-day test falls between 500 lbs. to 550 lbs.
- 10 % When the seven-day test falls between 550 lbs. to 600 lbs.
- 5 % When the seven-day test is 600 lbs. or upwards."

The cement-sand briquettes should bear the following tensile strains:—"Seven days from gauging, 150 lbs.; twenty-eight days from gauging, 250 lbs. The increase from seven to twenty-eight days shall not be less than 20 %."<sup>1</sup>

It is doubtful whether these restrictions are of any practical utility (Reid).

The neat tensile strength of cements is of considerably greater significance than that of cement-sand mixtures, because it affords an indication of the nature of the product. Portland cement, tested neat, has by far the highest tensile strength of all binding materials, but in the sand test it is often surpassed by Roman cement.

According to the German standard specification, briquettes are required to be kept for twenty-eight days before testing, viz., one day in air and twenty-seven days under water. The strength of neat Portland cement shall then be not less than 16 kilos per sq. cm. (227 lbs. per sq. in.).

In addition to making tests of the tensile strain after seven and twenty-eight days, it is also desirable to make tests at a shorter interval after gauging, say three days. A cement, for instance, which shows a tensile strain of 280, 420, and 640 lbs., after three, seven, and twenty-eight days respectively, is obviously of much better quality than one showing 440, 560, and 620 lbs. at the same periods, even though the final results be similar. A consideration of the two curves of time-hardening makes it clear that the last-named cement will reach its maximum strength after perhaps six months, whereas the former will continue to harden for perhaps two years. In addition to these periods, it is well, when possible, to test after three months, six months, one year, and two years, for thus only is it possible to obtain really instructive curves of strength.

**The Crushing Strain.**—The briquettes for the crushing test are made and treated in the same way as those for the tensile tests. As the crushing strength may be from twelve to fifteen times the tensile strength, a powerful hydraulic press is required to crush the cubes, which should have an area of about 50 sq. cm. on each side. The Amsler-Laffon press, in which the usual packing is replaced by a carefully

<sup>1</sup> *British Standard Specification*, p. 7.

ground piston lubricated by a special, viscous oil, is much used on the Continent.

A press of simpler construction is that of Weber, as improved by Schoch (Fig. 182), which consists of two pressure plates, the upper of which is raised or lowered by a hand-screw. This screw works in an iron girder which is connected to the lower part of the apparatus by two stays; at the lower end of the press is the cylinder containing the ram, which latter carries the other pressure plate and is held tight, with regard to the cylinder, by means of collars. In front of the apparatus are the arrangements for working the plunger and a pair of pressure-gauges. One of the gauges is graduated for high pressures, the other for lower pressures, such as are required with mortars and the like. The pressure produced by the plunger is communicated by the oil to the ram and to the gauges simultaneously, and is read off on the latter.

The periods of testing should be 3, 7, and 28 days, 3 and 6 months, and 1 and 2 years after preparation, both for neat and sand tests.

**The Adhesion.**—To carry out the adhesion test the cement is attached to an adhesion piece, which may be of stone, marble, ground glass, tile, etc. Michaëlis uses a special concrete made of one part of cement to two parts of sand. The adhesion piece is

placed at the bottom of a mould, which is filled up with the cement paste to be tested, and rammed by hand. A plate of glass is then laid on the top, the mould inverted, and the briquette pushed out by means of a wooden core. Michaëlis has devised special moulds for carrying out the test by his method, which greatly facilitate the preparation of briquettes.

This test has not become generally recognised; a muddy layer is formed at the junction of the cement and the adhesion piece, which materially affects the accuracy of the results.

The briquettes are treated exactly as for tensile strain, the testing machine being provided with special clips for the purpose.

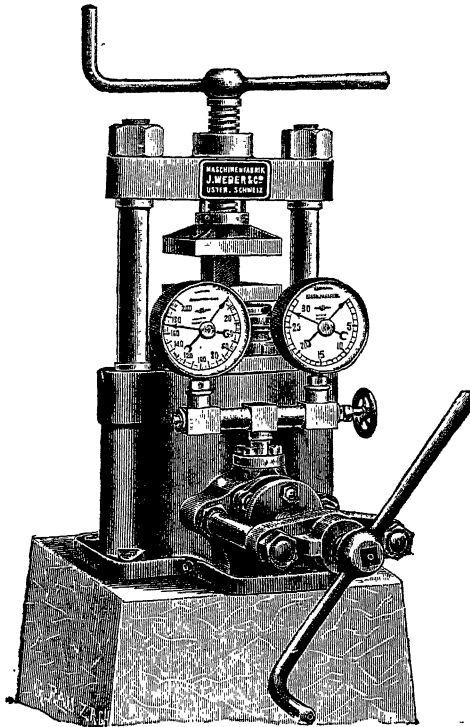


FIG. 182.

**The Bending Strain.**<sup>1</sup>—The tensile testing machine may be employed for this test, after being fitted with the auxiliary mechanism shown in Fig. 183. This consists of a strong steel bridge, A, which is fixed to a screw held in a ball-socket and occupies the position of the lower clip in the original apparatus. At each end of the bridge are oblong carriers, B B, in which are knife-edges which hold the ends of the briquette. Half-way between these is the third point of contact, a knife-edge fixed in the stirrup C and pressing against the under side of the test piece. By applying weights to the levers, force is exerted at C, until the test piece is snapped. The distance B B and the section of the briquette are of standard dimensions. Under ordinary circumstances a briquette of  $4 \times 4$  sq. cm. sectional area is used, which has the advantage of being suitable for the crushing test after being broken;

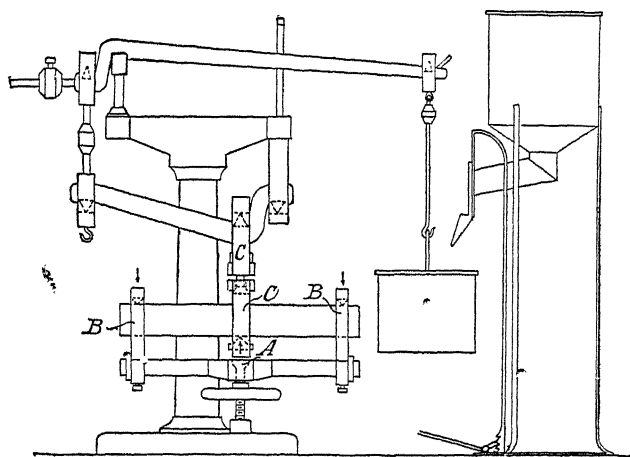


FIG. 183.

the distance between the outer knife-edges is 256 mm. Under these conditions the bending strain will be 30 times the load applied to the levers, working at the factor 50. The carriers B B can be moved inwards along the bridge until they are 100 mm. apart; in this position they serve for small briquettes of  $2 \times 2$  sq. cm. section. For such cases the central knife-edge must be raised 2 cm.; for this purpose it is constructed to slide between vertical grooves, so that it is merely necessary to place a steel block 2 cm. thick underneath it.

It is found, as a rule, that the bending strength of a cement is about double the tensile strength.

An excellent bending test apparatus has been adapted by Amsler-Laffon to their crushing machine, by means of which a maximum strain of 5000 kilos can be produced.

<sup>1</sup> Cf. Michaëlis, *Tonindustrie Zeit.*, 1898, 22, 408.

## ADULTERATIONS OF PORTLAND CEMENT

The manufacture of Portland cement has been so simplified and cheapened of late years that there are but few cases in which adulteration would be remunerative. Blast-furnace slag is practically the only substance that is likely to be used as an adulterant, and the chemical composition of this material is so similar to that of Portland cement that its detection by analysis is difficult. Many attempts have been made to limit the term "Portland cement" to a product obtained from certain materials manufactured by definite processes. Practically no cement is now made in the same way as that produced by Aspdin, the inventor, who first called his material "Portland cement." Strictly speaking, therefore, no cement now in the market is real "Portland" as defined by its originator; but consumers understand by the term a product possessing certain definite properties, and any mixture departing materially from the recognised standard should have its composition declared to the purchaser.

In order to obtain a process for detecting an admixture of blast-furnace slag with Portland cement, a special investigation was carried out by R. and W. Fresenius for the Association of German Portland Cement Manufacturers, but the chemical tests proposed were not considered conclusive, and were not adopted as standards.

The best means of detection is Hauenschild's flotation test, which is conducted, according to Loebell's method, as follows:—

The cement is first submitted to Fresenius' permanganate test, and its reducing effect determined. If 1 g. of the sample requires not more than 3 mg. of potassium permanganate, the absence of blast-furnace slag may be assumed. If a greater quantity is reduced, the material may consist either of (1) rotatory kiln cement, (2) cement mixed with blast-furnace slag, or (3) cement to which slag has been added before calcination. It is then advisable to make an analysis by flotation. For this purpose the cement is sifted through a sieve of 2500 meshes to the sq. cm. and 10 g. of the fine material stirred up with benzene in a flat crystallising dish and washed so as to remove the very finest dust; the residue is dried at 110°. To prepare the separating liquid, about 50 c.c. of methylene iodide (dried over calcium chloride and filtered through Portland cement which has been recently ignited and kept in a desiccator) are placed in a cylinder surrounded by water at 15° and rectified oil of turpentine (dried over calcium chloride and filtered) added drop by drop and well mixed, until the specific gravity of the liquid is 3.010. The liquid is kept in a yellow bottle to protect it from the action of light. This mixture is much less sensitive to light than a methylene iodide-benzene mixture, to which it is also superior in other respects. To carry out the test a dry separating funnel of about 70 c.c. capacity



(Fig. 184), the stopcock of which has been greased with vaseline, is charged with 40 to 50 c.c. of the separating liquid, and 5 g. of the prepared cement are introduced by means of a short-stemmed funnel. The separating funnel *t* is thoroughly shaken and evacuated to about 17 mm. of mercury by means of the filter-pump *n* during about five minutes; the evacuation should not be prolonged beyond this period, as otherwise some turpentine may evaporate and cause the liquid to change its density. It will be found necessary to open the pinchcock *q* from time to time, in order to guard against excessive frothing. The funnel, which must be carefully stoppered, is then laid on its side, gently agitated by rocking, and allowed to remain protected from light for a short time, until the lighter solids have collected at the top of the liquid and the heavier have settled at the bottom; the funnel is then held at the neck and very slowly raised into a vertical position. By proceeding in this manner, the lighter and heavier particles are enabled

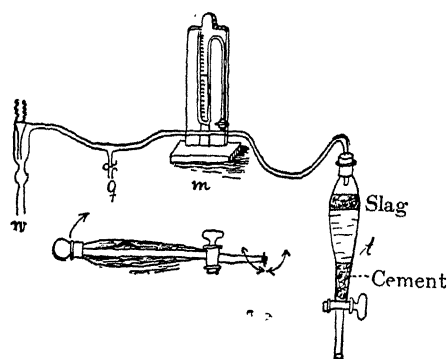


FIG. 184.

to pass one another, and those light particles which are retained by the heavy ones are given time to disengage themselves and to rise to the surface. A single treatment of the cement with the separating liquid thus affords an approximately quantitative separation of the constituents. The cement which sinks to the bottom is cautiously transferred to a Gooch crucible (Fig. 14, p. 26), in which it is dried and weighed. In

fitting up the crucible, a layer of chemically purified, long-fibre asbestos is laid on the bottom of the crucible, then a layer of short-fibre asbestos, then a porcelain filter-plate, and finally another layer of short-fibre asbestos. The crucible is then fitted up in the usual way, the layer of asbestos washed with distilled water, and the crucible dried at 110° and weighed. The separated cement is then filtered off. The clear methylene iodide mixture is removed from the filter flask and the residue in the crucible washed with absolute alcohol, benzene, and finally with ether, alternately, with and without suction. The crucible and its contents are dried at 110° and weighed, and the cement then subjected to chemical analysis.

The slag which rises to the top of the separating liquid is similarly treated. It is not desirable to use more than 5 g. of material for the valuation. The separating liquid must be readjusted to a density of 3.010 before each experiment, since a portion of the turpentine evaporates during filtration.

To recover the methylene iodide, the united washings are distilled to expel the less valuable solvents, and the residue cooled to  $5^{\circ}$ ; the iodide then separates out in white scales, from which the brown mother liquor is poured away. Under the action of light the distillate will be found to assume a pink tint due to a separation of iodine; this can be removed by shaking with and subsequently distilling over mercury, as mercuric iodide is soluble in the mixture of liquids used in the washing. It is imperative to follow the above directions exactly, if good results are to be obtained.

The products separated are:—

1. *Light Materials*, which float on the liquid and which may consist of:—

Carbon, average sp. gr. 1.39.

Gypsum, sp. gr. 2.33.

Coal-ash, average sp. gr. 2.73.

Blast-furnace slag, average sp. gr. 2.94.

These can be further separated from one another by treatment with suitably adjusted methylene iodide-turpentine mixtures.

2. *Heavy Materials*, which sink in the liquid and which may consist of:—

Cement, average sp. gr. 3.035.

Particles of iron, sp. gr. above 3.01.

Carbides from the slag, sp. gr. above 3.01.

These can also be separated by means of suitable liquids.

Chemical analysis of the separate portions yields trustworthy information as to the presence of slag. According to Tetmajer, blast-furnace slags of the most varied origin contain 27.31 to 39.95 per cent.  $\text{SiO}_2$  and 25.24 to 50.67 per cent.  $\text{CaO}$ , whilst the limits for Portland cement are 19 to 26 per cent.  $\text{SiO}_2$  and 57 to 66 per cent.  $\text{CaO}$ .

#### IV. GYPSUM

The analytical examination of the raw material is mainly concerned with the degree of purity of the gypsum. The methods employed are similar to those used for the analysis of cements.

Pure gypsum is calcium sulphate with two molecules of combined water,  $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ , and has therefore the percentage composition  $\text{CaO}$  32.56,  $\text{SO}_3$  46.51,  $\text{H}_2\text{O}$  20.93.

Dehydrated gypsum is a very quick-setting material, and is therefore invariably used when very quick-setting mortar is required. Properly burnt plaster of Paris should set hard in from three to four minutes. Since the last traces of water are only expelled at  $270^{\circ}$  to  $300^{\circ}$ , plaster burnt to the right degree still contains about 3 per cent. of water, corresponding to the semi-hydrate  $\text{CaSO}_4 \cdot \frac{1}{2}\text{H}_2\text{O}$ ; its specific gravity is

then 2.685, whereas fully dehydrated gypsum, or the naturally occurring anhydrite, has a specific gravity of 2.926.

The proportion of water (up to 3 per cent.) and the specific gravity thus afford the best means of distinguishing between the two commercial varieties of plaster of Paris. The commoner of these is lightly burnt plaster, used for mouldings and plaster, and, in a more carefully prepared form, for casting and modelling. The other variety is dead-burnt, *i.e.*, anhydrous plaster, which has lately come into great favour for flooring.<sup>1</sup>

The characteristic and distinguishing properties of the two varieties are as follows:—

*Colour.* Lightly burnt plaster has a bluish tinge; dead-burnt plaster is of a decidedly reddish-white tint.

*Specific Gravity.* Lightly burnt plaster has a specific gravity of about 2.7; that of dead-burnt plaster is 2.9.

*Weight.* A litre of lightly burnt plaster weighs from 650 to 850 g. loosely filled and from 1200 to 1400 g. shaken down. Dead-burnt plaster being denser and more coarsely ground, weighs from 1000 to 1100 g. and from 1500 to 1600 g. per litre respectively.

*Fineness.* Modelling plaster is the most finely ground product, and then stucco plaster; flooring plaster is comparatively coarse.

*Setting.* Lightly burnt plaster requires from one to one and a half parts of water to form a fluid paste. The test, unlike that applied to cement, is carried out by throwing the plaster into water, stirring rapidly, and pouring out the paste. Should a tendency to form lumps be observed, faulty calcination is indicated. Dead-burnt plaster requires only about half as much water, and yields a paste of the consistency of dough, like cement.

Lightly burnt plaster sets very rapidly. Setting can be retarded considerably by adding to the water either alcohol (10 to 20 per cent.) or borax, or nitrogenous substances such as size.

Dead-burnt plaster, on the other hand, sets exceedingly slowly; the time of setting varies between ten and fifty hours and averages from twelve to eighteen hours.

*Evolution of Heat in Setting* is shown very markedly by lightly burnt plaster, but not at all by dead-burnt plaster.

*Increase of Volume in Setting* is again a property of lightly burnt but not of dead-burnt plaster; it reaches about 1 per cent. with the former material.

*Blowing and Shrinkage* do not occur with either variety of plaster, if properly prepared.

<sup>1</sup> For details as to the five different modifications of calcium sulphate, *cf.* van't Hoff, *Chem. Centr.*, 1901, II., 142; 1902, I., 280; *Z. Electrochem.*, 1902, 8, 575; *Z. physik. Chem.*, 1903, 45, 257; *Roßland, Ber.*, 1900, 33, 2831; *Chem. Zeit.*, 1902, 26, 804; *Z. anorg. Chem.*, 1903, 35, 201; 1903, 36, 332.

*Hardness.* The quality of a plaster, especially of the lightly burnt class, can be readily tested by preparing a pat on a slab of glass, allowing it to set, and making a straight scratch with a knife on the under side; if the plaster is good it should break along the scratch, exactly like glass cut with a diamond.

*Mechanical Strength.* Lightly burnt plaster shows after twenty-eight days a tensile strength of about 20 kilos and a crushing strength of about 90 kilos per sq. cm. (284 and 1281 lbs. per sq. in. respectively). • Dead-burnt plaster attains considerably greater strengths; in experiments conducted by the Tonindustrie Laboratory at Berlin, crushing strengths up to 250 kilos to the sq. cm. (3557 lbs. per sq. in.) were observed.<sup>1</sup>

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<sup>1</sup> For a full account of these tests, cf. *Das kleine Gipsbuch*, published by the Tonindustrie Zeitung, Berlin.

## DRINKING WATER AND WATER SUPPLIES

By Professor L. W. WINKLER,<sup>1</sup> Budapest. English translation, revised by GILBERT J. FOWLER, D.Sc., Lecturer in Bacteriological Chemistry in the Public Health Department of the University of Manchester, Consulting Chemist to the Manchester Corporation Rivers Committee.

CHEMICALLY pure water does not occur in nature: all natural waters contain varying amounts of salts, etc., in solution. Glacier water is usually the purest form found; rain water is next in purity, but almost always contains, in addition to dissolved gases (nitrogen, oxygen, and carbon dioxide), ammonia (1 to 5 mgm. per litre), and traces of nitrous and nitric acids. Furthermore, rain carries down dust-particles, from which it extracts minute amounts of mineral constituents such as sodium chloride. Considerable quantities of inorganic constituents, especially sulphuric acid, are found in rain water collected in the neighbourhood of manufacturing towns; micro-organisms and their spores are also always present.

Rain, after falling, sinks into the ground to depths which vary with the nature of the latter, and reappears at the surface as spring water. Below the surface the water comes into intimate contact with mineral substances, varying proportions of which are dissolved. Though the earth's crust is mainly composed of substances almost insoluble in pure water, many such compounds are dissolved owing to the water which has penetrated the ground being charged with carbon dioxide derived from the air of the soil. All spring water consequently contains calcium and magnesium salts, which determine its hardness. Usually calcium and magnesium are mainly present as bicarbonates in natural waters and only in smaller amounts as sulphates; small amounts of sodium and potassium salts, sulphates, chlorides, and silicates are also similarly dissolved. Traces of carbon compounds, the nature of which is unknown, are also present in spring water, though the quantity of organic matter in pure, natural water is very small compared to that of the mineral constituents. Well-water is derived from an artificially opened

<sup>1</sup> In the writing of this section, use has been made of that by Prof. E. Eismann in the previous German edition and of the author's own publications.

spring, fed by ground water, and therefore contains the same constituents as spring water. Some spring waters are characterised by containing larger amounts of dissolved substances, or by having a higher temperature than those ordinarily found; they are then known as natural mineral waters.

After reaching the surface spring water continues its course as brook and river. Meanwhile it comes into contact with the air, which causes decomposition of the bicarbonates, liberation of carbon dioxide, and precipitation of the normal carbonates, which are almost insoluble. River water is therefore softer than spring water. River water also carries along small particles of minerals, such as clay, mica, and quartz, substances of vegetable and animal origin flushed down by rain, and living organisms. The river mud settles to the bottom as the flow becomes more equable, whilst the organic constituents are mineralised by the oxidising action of the atmosphere, assisted by micro-organisms, a process known as the self-purification of rivers.

This section is specially directed to the methods of examination employed for the hygienic valuation of water. Although most of these methods are identical with those used in the testing of water for technical purposes, processes especially suitable in the latter case will be dealt with, and their importance emphasised, in the next section.

Natural waters may be contaminated by various impurities. The sewers of towns usually empty into rivers, and the water of springs which are situated in the neighbourhood of cesspools or stables may be contaminated by urine and soluble faecal matter if the earth filtration is insufficient. Apart from the natural repugnance to the use of such water for drinking purposes, it is often directly injurious to health. Experience has shown that such water swarms with micro-organisms, amongst which disease germs may occur. Water is also often contaminated by various industrial works, particularly by factory effluent water (*cf.* "Sewage," p. 807); further, water conveyed by metal pipes may contain heavy metals in solution.

For the determination of the suitability of a water for drinking purposes, the physical and chemical examinations alone only suffice in exceptional cases; microscopic and bacteriological examinations can to-day hardly be dispensed with, and local inspection and geological examination are also of special importance, in order to decide with certainty on the purity or contamination of a water supply (*cf.* "Interpretation of Results," p. 793).

The value of a water analysis is largely dependent on correct sampling, as impurities may very easily be introduced from without by the use of imperfectly cleaned collecting vessels, old corks which have been previously used for other purposes, or dirty hands. For collecting samples only well-cleaned bottles of transparent glass should be used,

preferably provided with ground-glass stoppers. In taking water from wells provided with pumps, the sample must only be collected after pumping for some time; similarly, the water from supply pipes should be first allowed to run for some time, except in a case of supposed contamination by lead. Samples are taken from open streams by immersing the collecting vessel in the water; in this case both the surface water, which is often contaminated by dust, etc., and the muddy or sandy bottom, must be excluded. The collecting vessels must in every case be thoroughly rinsed with the water which is to be collected before being finally filled. The taking of the sample is best entrusted to an expert. Two litres usually suffice for a chemical examination. If the dissolved gases are to be determined, or a bacteriological examination to be undertaken, special precautions must be adopted in taking the sample (*cf.* pp. 776 and 790). If the water cannot be examined at once, it must be stored in a cool place, such as a cellar or ice-chest; specially constructed ice-boxes are made for the transportation of water samples for long distances.<sup>1</sup>

## THE EXAMINATION OF WATER

### PHYSICAL EXAMINATION

Water for drinking and domestic purposes is examined for temperature, clearness, colour, smell, and taste. Determinations of the specific gravity, or of the electrical conductivity, freezing-point, and osmotic pressure (calculated from the latter), such as are now generally made in the case of mineral water investigations, are not usually carried out.

#### Determination of Temperature.

This is carried out with a mercury thermometer graduated in  $\frac{1}{10}^{\circ}$ , the temperature of the atmosphere being also noted.

When it is impossible to reach the water directly, or to read off the thermometer, a large vessel is filled with the water and its temperature immediately taken. A minimum, or maximum, thermometer may also be used with advantage, according as to whether the temperature of the water or the atmosphere is the lower.

#### Clearness, Colour, Smell, and Taste.

*Clearness and Colour.* The clearness and colour of water are determined by pouring a sample into cylinders of colourless glass, 20 to 30 cm. high and about 4 cm. wide, placed on white paper. Absolutely

<sup>1</sup> For details regarding the taking of samples of water, *cf.* *The Examination of Waters and Water Supplies*, J. C. Thresh, 1904, p. 171; *Handbuch der Untersuchung und Beurteilung der Wässer*, Tiemann-Gärtner, 4th edition, 1895, p. 40.

colourless and clear water is kept for comparison. The shade and possible turbidity of the liquid are observed by looking into the cylinders from above.

A simple form of tintometer has been described by T. W. Burgess,<sup>1</sup> which is useful when a large number of samples of water of similar origin have to be compared. It consists essentially of two tubes, each 2 feet long, one of which is filled with distilled water and the other with the water under observation. The light passing through these is reflected upwards through two short cylinders, and the colour of the water matched with a standard coloured solution contained in the cylinder above the distilled water tube. The standard solution is made by dissolving 1 g. of crystallised cobalt sulphate and 0.05 g. of potassium bichromate in 1000 c.c. of water.

Humus substances impart to the water a yellowish, or yellow-brownish shade, which does not disappear on standing for some time, whereas turbidity caused by suspended impurities disappears either completely or partially on settling. Clay imparts a yellowish or greenish coloration, ferric hydroxide, precipitated by the air, a reddish-brown, calcium carbonate a white, and metallic sulphides, such as iron or lead sulphide, a black colour. Further knowledge of the quantity and character of the suspended matter may be obtained by microscopic examination, and also by filtration and subsequent examination of the residue by drying, weighing, and ignition. Very finely suspended matter may sometimes pass through good filter papers. The chemical examination of water should usually be preceded by thorough filtration if it is not quite clear.

In the report of the American Committee on Standard Methods of Water Analysis,<sup>2</sup> the turbidity standard adopted by the United States Geological Survey is recommended. This standard is represented by "a water which contains 100 parts of silica per million in such a state of fineness, that a bright platinum wire, 1 mm. in diameter, can just be seen when the centre of the wire is 100 mm. below the surface of the water, and the eye of the observer is 1.2 m. above the wire, the observation being made in the middle of the day, in the open air, but not in sunlight, and in a vessel so large that the sides do not shut out the light, so as to influence the results. The turbidity of such water shall be 100." Details as to the preparation of the standard silica, and the manner of making the comparisons are given in the Report.

*Smell.* To determine whether a water contains odorous substances, it is warmed to 40° to 50° in a large, half-filled flask. Any smell becomes noticeable on shaking the water round in the flask.

<sup>1</sup> *Analyst*, 1902, 27, 295.

<sup>2</sup> Report of Committee on Standard Methods of Water Analysis to the Laboratory Section of the American Public Health Association. Reprinted from *Journal of Infectious Diseases*, Suppl. No. 1, May 1905, pp. 16-19. Chicago, 1905.



*Taste.* To test for taste the water is warmed to 15° to 20°. Contamination by iron salts, coal-gas, and by products of mould-formation and decay, also by large quantities of common salt, can then be easily detected.

#### CHEMICAL EXAMINATION

The chemical examination of water may be more or less extensive. Determinations of the residue on evaporation, degree of hardness, reducing power, chlorine and albuminoid ammonia, together with qualitative tests for ammonia, sulphuric acid, and nitrous acid, are often sufficient, at least for hygienic purposes. A complete analysis is, however, fairly often required, whilst in some cases the determination of particular constituents, such as magnesia, iron, or lead, is the main essential.

It is still usual to express the results of water analyses in terms corresponding to the old dualistic formulæ. Thus a water is said to contain so much calcium oxide (CaO), magnesia (MgO), sulphur trioxide (SO<sub>3</sub>), nitric anhydride (N<sub>2</sub>O<sub>5</sub>), etc. So long ago as 1864, C. v. Than<sup>1</sup> proposed, for practical reasons, to express the results of mineral water analyses in terms of the amount of calcium (Ca), magnesium (Mg), sulphuric acid radical (SO<sub>4</sub>), nitric acid radical (NO<sub>3</sub>), etc. Modern investigations on the constitution of salt solutions have led to the conclusion that salts in dilute, aqueous solution are mainly dissociated into their ions, so that in the case of natural waters, the solution being very dilute, the salts are almost entirely dissociated; thus a natural water contains calcium ions (Ca<sup>++</sup>), magnesium ions (Mg<sup>++</sup>), sulphate ions (SO<sub>4</sub><sup>''</sup>), nitrate ions (NO<sub>3</sub><sup>'</sup>), etc., so that the earlier proposal of v. Than regarding the expression of results, is in complete harmony with the dissociation hypothesis. It would therefore be very desirable to express the results of drinking water analyses in accordance with v. Than's proposals, and the modern view of ionic dissociation; this would also accord with the suggestions put forward by W. Fresenius.<sup>2</sup> Meanwhile, however, the older method will be mainly followed in this section, in conformity with the majority of published analyses.

#### Residue on Evaporation.

The residue on evaporation contains all the inorganic and organic substances which were dissolved in the water, with the exception of those compounds which are volatile at relatively low temperatures. For the quantitative determination, from 250 to 1000 c.c. of water are evaporated

<sup>1</sup> "Über die zusammenstellung der Mineral-wasseranalysen," *Sitzungsber. d. Wiener k. Akademie*, 1865, vol. 51.—"Die chemische Konstitution der Mineralwässer und die Vergleichung derselben," *Tschermak's mineralog. und petrograph. Mitteilungen*, vol. 11, p. 487.

<sup>2</sup> *Fifth International Congress of Applied Chem.*, 1903.

carefully on the water-bath in a tared platinum or glass dish. To prevent dust particles from falling into the evaporating water, an inverted funnel (Fig. 10, p. 22), is fixed above the dish at a suitable height. After complete evaporation, the dish is removed from the water-bath and its outer surface cleaned with a soft, clean cloth; it is then dried in an air-oven for three hours at  $100^{\circ}$ , placed in a desiccator, allowed to cool, and weighed. The first weighing is often somewhat too high, as it always takes some time, and the residue is often hygroscopic. The drying and weighing are therefore repeated until a constant weight is obtained. The final weight is then multiplied by the necessary factor in order to express the weight of the residue in mg. per litre.

To obtain comparable results it is important always to dry the residue at the same temperature. Sell<sup>1</sup> has shown that slightly different values are obtained if the drying is carried out at  $100^{\circ}$ ,  $140^{\circ}$ , and  $180^{\circ}$ . The residue dried at  $100^{\circ}$  sometimes retains considerable quantities of water of crystallisation and hygroscopic moisture, as various inorganic salts, *e.g.* gypsum, magnesium sulphate, and especially calcium and magnesium chlorides, only lose all their water of crystallisation at higher temperatures, and mineral and organic compounds, precipitated in the amorphous state, sometimes retain hygroscopic moisture at  $100^{\circ}$ . In presence of considerable quantities of the above-mentioned salts, a more accurate result is therefore obtained if the temperature is raised to  $140^{\circ}$ , or better still to  $180^{\circ}$ . On the other hand, some substances present in the residue suffer partial decomposition at these temperatures.

To gauge the amount of organic matter present, the platinum dish containing the residue is more strongly heated over a naked flame. If the amount of organic matter is small, the residue acquires a faint yellow colour; if it is large in amount, the residue becomes brown or black. If the organic matter is mainly of vegetable origin, only a faint, non-characteristic smell is noticeable on decomposition, whereas nitrogenous organic matter, if present in considerable quantity, imparts a smell of singed horn to the fumes.

#### Alkalinity.

Recently collected spring or well water almost always shows a weakly acid reaction, due to the presence of free carbonic acid. Such water remains colourless on addition of a few drops of alcoholic phenolphthalein solution and a drop of lime water. If methyl orange is used as an indicator, most natural waters are apparently alkaline, for it is necessary to add a certain amount of hydrochloric acid in order to obtain a definite acid reaction; when this point is reached, all bicarbonates present are just converted into chlorides. If an indicator

<sup>1</sup> *Mitteilungen d. k. Gesundheitsamtes*, I., 1881.

is used which is sensitive to free carbonic acid, such as phenolphthalein, alizarin, or litmus, this point can only be obtained by vigorously boiling the water during the addition of the hydrochloric acid, and thus driving out the liberated carbon dioxide. The alkalinity of natural waters is to be regarded from this consideration.

According to Lunge<sup>1</sup> the alkalinity is more easily determined by using methyl orange as indicator, as it is then unnecessary to boil, and the use of glass vessels is permissible.

Two to three drops of aqueous methyl orange solution (1 to 1000) are added to 100 c.c. of the water, which is then titrated with  $N/10$  hydrochloric acid until the colour becomes reddish.

In the Report of the American Committee<sup>2</sup> lacmoid or erythrosine is recommended in preference to methyl orange.

As determinations of alkalinity are easily carried out on the spot, they are particularly suitable in the case of continuous investigations, in order to observe whether the composition of a water undergoes change. Also, the temporary hardness of a water (p. 740) and the amounts of half-combined and totally combined carbon dioxide (p. 762) can easily be calculated from the alkalinity.

### Acidity.

In the case of peaty waters, which are very generally acid, Houston<sup>3</sup> recommends lacmoid as a preliminary indicator; the merest trace of acid suffices to change the purplish-blue colour to a red colour.

The solution is best made by dissolving 0.2 g. of lacmoid in 100 c.c. of dilute alcohol (10 per cent.). A few drops added to 10 c.c. of the sample of water, contained in a sample tube, at once reveals the presence of the smallest trace of acid.

Moorland waters which give a neutral reaction with this indicator do not dissolve lead to any appreciable extent. Conversely, whenever a peaty water gives an acid reaction with lacmoid it will also be found to possess the power of acting as a solvent for lead.

If a water is found to give an acid reaction with lacmoid, the amount of the acidity is determined by titrating a definite quantity of the water with a decinormal solution of sodium carbonate (5.3 g.  $\text{Na}_2\text{CO}_3$  per litre). Phenolphthalein (0.5 g. in 100 c.c. of 50 per cent. alcohol) is used as indicator, as although open to some objections, it is found that comparable results are obtained. The results are expressed as acidity, in terms of c.c. of  $N/10$   $\text{Na}_2\text{CO}_3$  required to neutralise 100 c.c. of the water.

<sup>1</sup> *Die Wasserversorgung von Zürich*, 1885, p. 104.

<sup>2</sup> *Loc. cit.*, p. 61.

<sup>3</sup> *Thirteenth Annual Report of the Local Government Board*, 1900-01. Supplement in continuation of the Report of the Medical Officer for 1900-01, "On Lead-poisoning and Water Supplies," p. 67.

### Hardness.

English degrees of hardness (Clark's scale) are equivalent to grains of calcium carbonate per imperial gallon of 70,000 grains; multiplied by 1.43 they give parts per 100,000.

In Germany, degrees of hardness indicate the number of parts by weight of calcium oxide in 100,000 parts by weight of water, any magnesium compounds present being taken into account as equivalent quantities of calcium oxide. Thus, if a water is said to have a hardness of 10° it is concluded that in 100,000 parts by weight it contains calcium and magnesium as bicarbonates, sulphates, nitrates, and chlorides equivalent in amount to 10 parts by weight of calcium oxide.

In France, degrees of hardness indicate parts by weight of calcium carbonate in 100,000 parts of water.

Accordingly, 1 English degree of hardness = 0.8 German degrees and = 1.432 French degrees.

A water of less than 5 English degrees of hardness is considered soft, of between 5° and 15° moderately hard, and of over 15° as hard.

For the accurate determination of the hardness of a water, the content of calcium and of magnesium is estimated gravimetrically (*cf.* p. 405). Each centigramme of calcium oxide found in 1 litre of water corresponds to 1 part per 100,000; the number of centigrammes of magnesium oxide found per litre multiplied by 1.4 gives its equivalent in calcium oxide. The total hardness is the sum of the hardness due to calcium and magnesium oxides.

Hardness can also be satisfactorily determined by alkalimetry. In Wartha's form of this method<sup>1</sup> the alkalinity of the water is first determined, with alizarin as indicator. This indicator, which on account of its sensitiveness to carbonic acid necessitates titration in boiling solution, is added to 100 c.c. of the sample and titrated, boiling with *N*/10 hydrochloric acid until the violet colour changes to a clear yellow, which persists on continued boiling. The neutralised water is then treated with an excess of a solution consisting of equal parts of *N*/10 sodium hydroxide and *N*/10 sodium carbonate solutions, boiled for some minutes, cooled, diluted to 200 c.c., filtered, and the excess of alkali determined in 100 c.c. of the filtrate by titration with *N*/10 hydrochloric acid, methyl orange being used as indicator. The number of c.c. of *N*/10 alkali used, multiplied by 3.5, gives the total hardness in English degrees.

A simpler plan in employing this method is to use only one indicator, namely, methyl orange. After determining the alkalinity at the

<sup>1</sup> *Cf.* J. Pfeifer, *Z. angew. Chem.*, 1902, 15, 198; also, H. R. Procter, *J. Soc. Chem. Ind.*, 1904, 23, 8.

ordinary temperature, the liquid is heated to boiling,  $N/10$  sodium hydroxide and carbonate solution added in excess, and the estimation continued as above.

Mohr, and subsequently Hehner, recommend titration with  $N/50$  sodium carbonate and  $N/50$  sulphuric acid; lacmoid, according to Sutton,<sup>1</sup> being the best indicator. The temporary hardness is obtained by heating 100 c.c. of the water to boiling, and adding the standard acid cautiously in presence of the indicator till the change of colour occurs. The number of c.c. of acid used represent the number of Clark's degrees of temporary hardness per 100,000 parts of water. The permanent hardness is ascertained by taking 100 c.c. of the water, and adding to it a rather large, measured excess of the standard sodium carbonate. The whole is then evaporated in a platinum dish to dryness, the soluble portion extracted with small quantities of distilled water, filtered through a very small filter paper, and the excess of sodium carbonate determined in the filtrate by titration with the standard acid: the volume of sodium carbonate solution decomposed represents the permanent hardness.

**Clark's Soap Test.**—For many technical and most hygienic analyses of water an approximate determination of the hardness is sufficient, and is usually carried out by means of a titrated soap solution. Of the methods on this basis, that of Clark<sup>2</sup> is the best known and most widely adopted, although as Lunge has pointed out, it frequently gives wrong results, and also takes longer to carry out than the more exact methods described above.

The following description of the method is taken from the Report of the American Committee on Standard Methods of Water Analysis.<sup>3</sup>

*Reagents:* 1. *Standard Calcium Chloride solution.* Dissolve 0.2 g. of pure calcite (calcium carbonate) in a little dilute hydrochloric acid, being careful to avoid loss of solution by spiriting. Evaporate to dryness several times to expel excess of acid, dissolve the residue in distilled water, and make up to 1 litre. One c.c. is equivalent to 0.0002 g. of calcium carbonate.

2. *Standard Soap solution.* Dissolve 100 g. of dry, white Castile soap in 1 litre of 80 per cent. alcohol, and allow the solution to stand several days before standardising. From the above stock solution, dilute with 70 per cent. alcohol such a quantity that the resulting diluted soap solution will give a permanent lather when 6.40 c.c. of it are properly added to 20 c.c. of the standard calcium chloride solution. Usually from 75 c.c. to 100 c.c. of the stock soap solution are required for making 1 litre of the standard soap solution. Pure potassium soap made from lead plaster and potassium carbonate may be used with advantage in place of Castile soap.

<sup>1</sup> *Volumetric Analysis*, 9th edition, 1904, p. 70.

<sup>2</sup> *Jahresber. f. Chemie*, 1850, p. 608.

<sup>3</sup> *Loc. cit.*, p. 55.

For the standardisation, 20 c.c. of the calcium chloride solution are placed in a 250 c.c. glass-stoppered bottle and diluted to 50 c.c. with distilled water which has been recently boiled and cooled. The soap solution is then added from a burette in portions of 0.2 or 0.3 c.c. at a time, shaking the bottle vigorously after each addition, until a lather is formed over the entire surface of the water which persists for five minutes after the bottle is laid upon its side. If the soap solution is of the strength stated above, the quantity of calcium carbonate equivalent to each c.c. of the soap solution is given by the following table:—

Table of Hardness, showing the parts per 100,000 of Calcium Carbonate ( $\text{CaCO}_3$ ) for each Tenth of a Cubic Centimetre of Soap Solution when 50 c.c. of the Sample are used.

c.c. of Soap Solution.	0.0 c.c.	0.1 c.c.	0.2 c.c.	0.3 c.c.	0.4 c.c.	0.5 c.c.	0.6 c.c.	0.7 c.c.	0.8 c.c.	0.9 c.c.
0.0	...	...	...	...	...	...	...	0.0	.16	.32
1.0	.48	.63	.79	.95	1.11	1.27	1.43	1.56	1.69	1.82
2.0	1.95	2.08	2.21	2.34	2.47	2.60	2.73	2.86	2.99	3.12
3.0	3.25	3.38	3.51	3.64	3.77	3.80	4.03	4.16	4.29	4.43
4.0	4.57	4.71	4.86	5.00	5.14	5.29	5.43	5.57	5.71	5.86
5.0	6.00	6.14	6.29	6.43	6.57	6.71	6.86	7.00	7.14	7.29
6.0	7.43	7.57	7.71	7.86	8.00	8.14	8.29	8.43	8.57	8.71
7.0	8.86	9.00	9.14	9.29	9.43	9.57	9.71	9.86	10.00	10.15

This table does not provide for the use of as large a volume of soap solution for a single determination as was formerly the case, owing to the fact that the end-point becomes somewhat obscured in the presence of magnesium salts, as explained below, when more than about 7 c.c. are used.

*Method of Determination.* Measure 50 c.c. of the water into a 250 c.c. bottle and add soap solution in small quantities at a time and in precisely the same manner as described under the standardisation of the soap solution. From the result obtained the total hardness of the water in terms of calcium carbonate is given by the above table.

When adding the soap solution to waters containing magnesium salts, it is necessary to avoid mistaking the false or magnesium end-point for the true value. Consequently, after the titration is apparently finished, read the burette and add about 0.5 c.c. more of soap solution. If the end-point was due to magnesium, the lather disappears. Soap solution must then be added until the true end-point is reached. Usually the false lather persists for less than five minutes.

When more than 7 c.c. of soap solution are required for 50 c.c. of the water, it is necessary to take less of the sample and dilute to 50 c.c. with distilled water which has been recently boiled and cooled. This

dilution also reduces somewhat the disturbing influence of magnesium salts, which take up more soap than the equivalent weights of calcium salts.

At best, the soap method is not a precise test, on account of the varying amounts of calcium and magnesium salts present in different waters. For hard waters, especially in connection with processes for purification and softening, the method should not be used.

A method similar to that of Clark, which allows of the rapid estimation both of the total hardness and of that due to calcium and to magnesium salts individually, has been described by L. W. Winkler.<sup>1</sup>

The above methods give the *total hardness* of the water. On boiling, the greater part of the bicarbonates of calcium and magnesium contained in the water are precipitated as carbonates, whilst the sulphates, nitrates, and chlorides remain in solution. The water therefore becomes softer on boiling, and the hardness of the boiled water, after dilution to its original volume with distilled water, is called the *permanent hardness*. The difference between the total hardness and the permanent hardness is known as the *temporary hardness*. The last corresponds approximately to the originally dissolved bicarbonates of calcium and magnesium.

To determine the permanent hardness by Clark's method, the water to be examined is boiled for some time, brought to its original volume, filtered, and the hardness of the filtrate determined. The value for the permanent hardness thus obtained is, however, an empirical figure, as the decomposition of the bicarbonates is not complete. The actual amount of bicarbonate present is more simply arrived at by calculating the temporary hardness from the alkalinity of the water (1 c.c. of *N*/10 hydrochloric acid per 100 c.c. water being equal to 3.5 English degrees), and subtracting this from the total hardness.<sup>2</sup>

In the case of mineral waters, and of boiler-feed waters which have been softened with an excessive quantity of sodium carbonate, the temporary hardness calculated from the alkalinity may be apparently greater than the total hardness; in this case the water has of course no permanent hardness, and contains sodium carbonate in excess. This has also been found to be the case in numerous samples of water obtained from the chalk below the London clay,<sup>3</sup> and in Yorkshire waters.<sup>4</sup>

### Reducing Power or "Oxygen Absorption."

In the purer natural waters the quantity of organic matter present is usually only minute, and consists essentially of products of de-

<sup>1</sup> *Z. anal. Chem.*, 1901, 40, 82; *Z. angew. Chem.*, 1903, 16, 200.

<sup>2</sup> Cf. J. Pfeifer, G. Lunge, and also H. R. Procter, *loc. cit.*

<sup>3</sup> W. W. Fisher, *Analyst*, 1901, 26, 202.

<sup>4</sup> H. R. Procter, *J. Soc. Chem. Ind.*, 1904, 23, 8.

composition of vegetable remains; these contain, as a rule, little nitrogen, and are known as "Humus substances." On the other hand, highly nitrogenous decomposition-products of animal refuse and remains of metabolic products of the animal organism also occur, more particularly in waters which are exposed to surface impurities, or which come into contact with polluted ground. The organic compounds of this character vary greatly in properties. Some are easily oxidised and easily decomposed, whilst others are stable and are oxidised only with difficulty; some are volatile with water vapour at relatively low temperatures, others remain behind when the water is evaporated; finally, some are basic, whilst others are acidic in character. Their importance, from an hygienic standpoint, also varies greatly. Whilst the organic substances derived from vegetable remains may in general be considered as hygienically indifferent, the presence of nitrogenous decomposition-products from animal organisms make the character of a water highly suspicious.

The quantitative estimation of the individual organic compounds in water offers great, and in part, insuperable difficulties, both on account of their variety and also because their composition is in many cases still unknown. The determination is accordingly at present restricted to ascertaining whether a water contains serious quantities of organic impurities, and whether these are mainly of vegetable or of animal origin. From a purely hygienic standpoint, the second question is the more important.

As it is impossible to determine the quantity of organic compounds in water directly, an indirect method is adopted, which consists in estimating its reducing power; an approximate valuation of the content of organic matter is thus obtained.

An approximate differentiation of the nature of the organic impurities is effected by separating and estimating the nitrogen in the form of the so-called "Albuminoid" or of the "Proteid-Ammonia."

The determination based on the oxidation of the organic matter will be considered first; the determination of albuminoid and of proteid-ammonia is described later (p. 769).

The reducing power of a natural water is determined by means of potassium permanganate; either an acid (Kubel's and Tidy's methods) or an alkaline (Schulze's method) permanganate solution may be used. Opinion is much divided as to which of these methods is the better, and also as to the best means of carrying them out.

According to L. W. Winkler,<sup>1</sup> all experience is decidedly in favour of oxidation in alkaline solution, partly because the oxidation of the organic substance is usually more complete, and the presence of considerable amounts of chlorides has no disturbing effect, and also

<sup>1</sup> *Z. anal. Chem.*, 1902, 41, 419.



because the alkaline liquid can be maintained at the boil with incomparably more ease than the acid solution. This seemingly minor detail is of importance, as it is almost impossible, after driving out the dissolved gases, to maintain the acidified water at the boil in the case of a pure water; superheating and percussive ebullition alternate, and may easily lead to loss. The following solutions are required for the determination:—

1. *Dilute Sulphuric acid.* One hundred c.c. of purest commercial sulphuric acid are poured into 300 c.c. of distilled water contained in a flask. Dilute potassium permanganate solution is then added drop by drop to the liquid, which has previously been partially cooled, but must still be fairly warm, until it has acquired a just perceptible, permanent pink colour.

2. *Oxalic acid solution.* Commercial oxalic acid is recrystallised, first from water containing hydrochloric acid, and then from pure distilled water. It is then dried in the air at the ordinary temperature until the crystals do not adhere together. 0.630 g. of this pure acid are dissolved in distilled water, with addition of 10 c.c. of the above dilute sulphuric acid solution, and the whole diluted to 1 litre; this gives an  $N/100$  oxalic acid solution. The solution must be kept in the dark; it keeps practically unchanged for a year, the alteration in strength not being more than about 0.5 per cent.<sup>1</sup>

3. *Alkaline Potassium Permanganate solution.* Fifty g. of pure sodium hydroxide and 0.8 g. of potassium permanganate are dissolved in 250 c.c. of distilled water at 60° to 70°, the solution diluted to 500 c.c. after it has cooled completely, and kept in a well-closed bottle; 100 c.c. of this solution are then diluted to 500 c.c. for use. The strength of the solution is determined by titrating with 10 c.c. of the  $N/100$  oxalic acid solution, acidified with 10 c.c. of the dilute sulphuric acid, in a very small flask. If so much permanganate is used in the titration that the liquid is turned just perceptibly pink, 0.05 c.c. must be deducted as a correction. The colour of the liquid is observed by holding the flask over a sheet of milk-glass. The permanganate solution is measured from a narrow burette with a glass tap lubricated with vaseline.

\* *Method of Determination.* One hundred c.c. of the sample are placed in a 300 c.c. conical flask, and 10 c.c. of  $N/100$  permanganate solution added; the flask is then heated on an asbestos card until the liquid boils, when the flame is regulated so that it continues to boil quietly and uniformly. After the liquid has boiled for ten minutes the flask is removed from the flame, and 10 c.c. of dilute sulphuric acid immediately added with shaking, followed at once by 10 c.c. of  $N/100$  oxalic acid solution. After some minutes, when the liquid has become

<sup>1</sup> Others regard this solution as less stable. Cf. Beck, p. 95.

perfectly colourless, alkaline permanganate solution is added drop by drop from the burette until the solution is just perceptibly pink; 0.1 c.c. of  $N/100$  permanganate solution suffices to perceptibly colour 100 c.c. of liquid, and the loss of oxygen by boiling is equivalent to 0.2 c.c., so that the total correction to be made consists of a deduction of 0.3 c.c. of the permanganate solution. If the water under investigation contains appreciable quantities of nitrous acid or of ferrous salts, the amount of permanganate solution necessary for their oxidation must also be deducted. If the water reduces more than 5 c.c. of the permanganate solution it must be correspondingly diluted with quite pure or distilled water of known reducing power before the final estimation.

The method as described above gives constant and concordant results if the instructions are carefully followed, but not if the conditions are varied. It must be borne in mind, however, that equal quantities of potassium permanganate used do not necessarily imply that the same amount of organic matter is present, as different organic substances have very different reducing powers.

It is usual to express the amount of organic impurity in water in terms of the amount of potassium permanganate used, or of oxygen necessary for its oxidation, calculated on either 1000 or 100,000 parts of water. As both hardness and alkalinity are expressed in degrees, it would be convenient, if only in order to avoid calculation, to express the reducing power in the same manner, that is, in degrees corresponding to the number of c.c. of  $N/100$  permanganate solution reduced by 100 c.c. of the water.

In England and America acid permanganate is generally used either at the boiling temperature, followed by titration with oxalic acid (Kubel), or at the ordinary temperature, followed by titration with potassium iodide and sodium thiosulphate. The Kubel method generally gives the higher figures, and as in the case of the method described above, the results vary according to the details of procedure employed.

The following details for the oxidation in acid solution are taken from the Report of the American Committee.

*Reagents:* 1. *Dilute Sulphuric acid.* One part of sulphuric acid to three parts of distilled water. This shall be freed from oxidisable matters by adding potassium permanganate until a faint pink colour persists after standing several hours.

2. *Standard Potassium Permanganate solution.* Dissolve 0.4 g. of the crystalline salt in 1 litre of distilled water. Standardise against an ammonium oxalate solution. One c.c. is equivalent to 0.0001 g. of available oxygen.

3. *Ammonium Oxalate solution.* Dissolve 0.888 g. of the substance

in 1 litre of distilled water. One c.c. is equivalent to 0.0001 g. of oxygen.

4. *Potassium Iodide solution.* Ten per cent. solution free from iodate.

5. *Sodium Thiosulphate solution.* Dissolve 1.0 g. of the pure crystallised salt in 1 litre of distilled water. Standardise against a potassium permanganate solution which has been standardised against an ammonium oxalate solution. As this solution does not keep well, determine its actual strength at frequent intervals.

6. *Starch Indicator.* Mix a small amount of clean starch with cold water until it becomes a thin paste, and stir this into 150 to 200 times its weight of boiling water. Boil for a few minutes, then sterilise. The solution may be preserved by adding a few drops of chloroform.

*Method of Determination.* Measure into a flask 100 c.c. of the water, or a smaller, diluted portion if the water is of high organic content. Add 10 c.c. of sulphuric acid solution and 10 c.c. of potassium permanganate solution, and allow the treated sample of water to digest in accordance with the detailed procedures carried out under differing conditions, as set forth below under the heading, "Period and Temperature of Digestion."

At the end of the period of digestion, remove the flask at once, and if the boiling temperature is used, add 10 c.c. of the ammonium oxalate solution. Titrate with the permanganate solution until a faint but distinct colour is obtained.

Each c.c. of the permanganate solution used, in excess of the oxalate solution, represents 0.0001 g. of oxygen consumed by the sample.

At the end of the period of digestion, if not made at the boiling temperature, add 0.5 c.c. of potassium iodide solution to discharge the pink colour, mix, and titrate the liberated iodine with thiosulphate until the yellow colour is nearly destroyed; then add a few drops of starch solution and continue the titration until the blue colour is just discharged.

Should the volume of permanganate solution be insufficient for complete oxidation, repeat the determination, using a larger volume, so that at least 3 c.c. of the permanganate solution will be present in excess when the ammonium oxalate solution is added.

When unoxidised mineral substances, such as ferrous sulphate, sulphides, nitrites, etc., are present in the sample, corrections should be applied as accurately as possible, by methods suitable for the samples analysed. Direct titration of the acidified sample in the cold, using a three-minute period of digestion, serves this purpose quite well for polluted surface waters and fairly well for purified sewage effluents. In all samples containing both unoxidised mineral compounds and gaseous organic substances, the latter should be driven off by heat and

the sample allowed to cool before applying this test for the correction factor.

Where such corrections are necessary the fact should be stated, with the amount of the correction.

*Period and Temperature of Digestion.* Unfortunately, widely varying details are practised in this respect.

1. Bring the acidified sample to the boiling-point, add the permanganate solution, and digest for two minutes at a boiling temperature. This procedure is facilitated by agitating the liquid constantly with a small current of air, to guard against bumping.

2. Same method as No. 1, except that the period of digestion is five minutes instead of two minutes.

3. Same method as No. 2, except that the permanganate solution is added to the acidulated sample when cold, and the period of digestion continued for five minutes after the sample reaches the boiling-point. The advantage of this method is that the oxygen-consuming powers are determined of the volatile matters present in some samples of sewage and of sewage effluents, which are driven off by heat and thus escape when analyses are made in accordance with the first two methods.

4. Same method as No. 3, except that the period of digestion is ten minutes instead of five minutes.

5. The permanganate is added in the cold to the acidulated sample and the flask placed immediately in a bath of boiling water, the water-level of which is kept above the level of the contents in the flask. Digestion is continued for exactly thirty minutes.

6. Digestion of the sample after the acid and permanganate solutions are added at approximately the room temperature, apparently to guard against decomposition of permanganate in the presence of much chlorine, for periods of three minutes, fifteen minutes, and four hours; many observers record the oxygen consumed after each of the three periods, while others record the result only for the four hours period. This method is adopted in England and to some extent abroad.

*Conclusions.* After careful consideration of the matter the views of the committee are as follows:—

1. From a strictly scientific standpoint the thirty-minute period of digestion at boiling temperature in a water-bath appears to give the most satisfactory results as regards uniformity and freedom from personal errors of manipulation. It is believed that where practicable this is the most satisfactory method.

2. Where samples from a given source are repeatedly analysed, it is advised that there be placed on record, for purposes of comparison, representative results by each of the methods of digestion above mentioned.

3. In connection with sewage works analysis, to which the utility of

this method is principally confined, it is recommended that the permanganate solution be added to the sample before heating, in order to include the oxygen consumed by volatile compounds.

### Silica.

Silica is usually present in natural waters in only very small quantities. It is of no importance from a hygienic standpoint, but the presence of appreciable quantities of silica becomes a consideration in the case of the analysis of water for technical purposes, as it is one of the substances which give rise to boiler incrustations.

To determine silicic acid, from 500 to 1000 c.c. of the water are acidified with hydrochloric acid and evaporated to dryness. The residue is moistened several times with hydrochloric acid, completely evaporated after each addition, and then dissolved in hot water with addition of hydrochloric acid. The silicic acid, which forms flocculent particles, is collected on a small filter, washed successively with dilute hydrochloric acid and with hot water, ignited, and weighed as silica. The filtrate may be used for the gravimetric estimation of sulphuric acid, or of calcium and magnesium.

If the sample contains much calcium sulphate it may be retained by the precipitated silica. In this case the impure silica is fused with ten times its weight of fusion-mixture and the silicic acid again separated.

### Sulphuric Acid.

For the qualitative detection of sulphuric acid, about 10 c.c. of the water are acidified with hydrochloric acid and a few drops of barium chloride solution added. If the water contains 100 mg.  $\text{SO}_3$  per litre, a white powdery precipitate is formed at once; 10 mg.  $\text{SO}_3$  per litre give a white turbidity after some minutes; 2 mg.  $\text{SO}_3$  per litre give a scarcely perceptible turbidity after standing for a considerable time.

The quantitative, gravimetric estimation of sulphuric acid depends on the same reaction. From 500 to 1000 c.c., or from 200 to 300 c.c. are taken for the estimation, according as to whether the qualitative test gave a turbidity or a considerable precipitate. The sample is acidified with hydrochloric acid and evaporated to dryness on the water-bath; should considerable quantities of nitrates be present a glass dish must be used for this purpose, as platinum is attacked. The residue is moistened with dilute hydrochloric acid, dissolved in about 50 c.c. of hot, distilled water, the silica filtered off and washed with 50 c.c. of hot water, and the filtrate precipitated with barium chloride, after the addition of ammonium chloride solution (*cf.* p. 274).

For technical and hygienic purposes an approximate determination of the sulphuric acid is sufficient; this can be quickly carried out colorimetrically. The principle of the method consists in decomposing

the dissolved sulphate with excess of barium chromate in hydrochloric acid solution, then neutralising the liquid with sodium hydroxide, filtering, and finally determining the amount of chromic acid in the filtrate colorimetrically; this is equivalent in quantity to the amount of sulphuric acid originally present.<sup>1</sup>

The barium chromate is prepared by adding an excess of potassium chromate solution to a solution of barium chloride acidified with a few drops of acetic acid. The precipitate is first washed by decantation, then thoroughly on the filter, dried, and ground to a powder. The chromate can also be kept under water. Five to ten drops of the shaken-up, turbid liquid are taken for use.

To carry out the estimation, from one hundred and fifty to two hundred c.c. of the water under examination are poured into a flask and acidified with 5 to 10 drops of fuming hydrochloric acid. 0.1 to 0.2 g. of pure barium chromate are then added, and the solution heated just to boiling, over the free flame. After cooling completely, sodium hydroxide solution is added until the liquid just turns red litmus paper faintly blue; a larger excess of sodium hydroxide is to be avoided. Finally the liquid is vigorously shaken, allowed to stand for a few minutes, and poured through a dry double filter paper; the first portions of the filtrate, which are usually turbid, are rejected, and the later, perfectly clear portions used for the determination. One hundred c.c. of the filtrate are poured into a cut-glass bottle, and 100 c.c. of distilled water, to which a few drops of sodium hydroxide solution are added, poured into a similar bottle for comparison. Potassium bichromate solution is then added from a burette to the contents of the second bottle until the colours of the two solutions correspond. The colour comparison may also be carried out in glass cylinders about 20 cm. high and 4 cm. wide. If 0.7 c.c. are deducted from the amount of potassium bichromate solution used, to allow for the amount of dissolved barium chromate, and the remainder multiplied by 10, the weight of  $\text{SO}_3$  is obtained in mg. To express the result in terms of  $\text{SO}_4$  the result is multiplied by 1.2.

The potassium bichromate solution is prepared by dissolving 1.839 g. of the pure salt in water and making up to 1 litre; each c.c. of this solution represents 0.0001 g.  $\text{SO}_3$ .

If the water contains considerable quantities of organic matter, some of the chromic acid is reduced, and less sulphuric acid found than is actually present. In such cases the organic matter must be destroyed before determining the sulphuric acid. For this purpose a measured quantity of the water, for instance 200 c.c., is treated with 5 to 10 drops of fuming hydrochloric acid and a few c.c. of strong chlorine water.

<sup>1</sup> Cf. L. W. Winkler, *Z. anal. Chem.*, 1901, 40, 467; also, Hartleb, *Chem. Centr.*, 1901, II 320; and Rossi, *ibid.*, 1902, II., 1272.

the excess of chlorine is then boiled off, the liquid cooled, diluted to its original volume, and the sulphuric acid then determined as described above.

### Chlorine.

Chlorine is tested for qualitatively by adding a few drops of nitric acid and silver nitrate solution to about 10 c.c. of the sample. The amount of chlorine present can be approximately estimated from the intensity of the reaction: 100 mg. of chlorine per litre produce a milky liquid from which silver chloride separates in flocks on shaking; 10 mg. per litre give a strongly opalescent liquid and 1 mg. per litre a very faint opalescence.

The quantitative estimation of chlorine may be made either gravimetrically or volumetrically by the usual methods (*cf.* p. 123).

L. W. Winkler<sup>1</sup> has modified Mohr's volumetric method, for the purpose of water analysis, by determining experimentally the amount which must be deducted from the volume of silver nitrate solution used to allow for the volume required for the coloration of the indicator. If a silver nitrate solution is employed, of which 1 c.c. is equivalent to 1 mg. of chlorine, and 1 c.c. of a 1 per cent. potassium chromate solution is used as indicator, and the determinations are carried out with 100 c.c. of water, then the necessary corrections are given by the following table:—

Silver Solution used, in c.c.	Deduction, in c.c.	Silver Solution used, in c.c.	Deduction, in c.c.	Silver Solution used, in c.c.	Deduction, in c.c.	Silver Solution used, in c.c.	Deduction, in c.c.
0.2	-0.20	0.7	-0.38	3.0	-0.46	7.0	-0.54
0.3	-0.25	0.8	-0.39	4.0	-0.48	8.0	-0.56
0.4	-0.30	0.9	-0.40	5.0	-0.50	9.0	-0.58
0.5	-0.33	1.0	-0.41	6.0	-0.52	10.0	-0.60
0.6	-0.36	2.0	-0.44				

In presence of large quantities of organic matter, which, though seldom present in a domestic water supply, may easily occur in a works' supply, a direct titration with silver nitrate is impossible, as the end of the reaction is obscured by the colour of the sample. In such cases the organic matter must be destroyed before titration. To effect this, 200 c.c. of the water are warmed to about 100°, and neutral potassium permanganate solution added until the water is faintly red in colour; it is then boiled for about five minutes, when, if the colour is destroyed, a few more drops of permanganate solution are added. The hot liquid is then treated with a few drops of alcohol to remove the excess of permanganate, allowed to stand for a quarter of an hour,

<sup>1</sup> *Z. anal. Chem.*, 1901, 40, 596.

the precipitated manganese compounds filtered off, and the filtrate, after allowing to cool, diluted to 200 c.c.; the solution, which must be neutral, is then divided into two equal portions and titrated. The same procedure is adopted if the water contains sulphuretted hydrogen.

In presence of large quantities of organic matter, the chlorine may be determined in the residue on evaporation, after first removing the organic matter by careful ignition. The residue is dissolved in as little cold, distilled water as possible, with addition of a few drops of nitric acid, the liquid filtered, a few crystals of potassium bicarbonate dissolved in it (an excess does not matter), and the chlorine titrated in the usual way.

### Iodine.

The occurrence of iodine in combination with albumins in the secretions of the thyroid gland having drawn attention to its great physiological importance, the presence of iodine in drinking waters has become of interest as a possible source of the supply of this element to the system.

To detect iodine in water, and simultaneously to determine its approximate amount, 1000 c.c. of the sample are treated with a few drops of sodium hydroxide solution, evaporated down to about 10 c.c., filtered into a wide test-tube, and the residue washed with about 5 c.c. of water. The combined filtrate and washings are acidified with hydrochloric acid, a drop of potassium nitrite solution added, followed by 5 c.c. of chloroform, and the whole vigorously shaken. Should the water contain 0.1 mg. of iodine, the chloroform is at once coloured pink. To approximately estimate the amount of iodine present, 15 c.c. of distilled water are placed in a second test-tube, 5 c.c. of chloroform, a few drops of hydrochloric acid, and a drop of nitrite solution added, and then a very dilute potassium iodide solution, of which 1 c.c. = 0.1 mg. iodine; the addition of the iodide solution is continued until, on shaking, the chloroform is coloured to the same extent as in the case of the sample under examination.

For the exact determination of small amounts of iodine the method described by Węszelszky<sup>1</sup> may be used.

### Nitric Acid.

The most suitable test for the detection of nitric acid in natural waters is the coloration produced by brucine and sulphuric acid.

About 1 c.c. of the water is added drop by drop to 3 c.c. of concentrated sulphuric acid, and after cooling completely, a few mg. of brucine are added to the solution. From the intensity of the colour one can judge whether much, little, or only traces of nitric acid are

<sup>1</sup> *Z. anal. Chem.*, 1900, 39, 85.



present. One hundred mg. of  $N_2O_5$  per litre cause a cherry-red coloration, which soon changes to orange and then to a sulphur-yellow on long standing; 10 mg. per litre give a rose-red solution, which changes to pale yellow on long standing; and 1 mg. per litre gives a pale rose-coloured solution, which becomes almost colourless on standing.

If the brucine is dissolved in the liquid whilst the latter is still hot, the coloration changes to yellow almost immediately.

The sulphuric acid used must be pure and free from nitric acid, or at most only contain a minute trace. It is absolutely necessary therefore to make a blank experiment with distilled water, sulphuric acid, and brucine; the absence of nitric acid in the sample can only be regarded as proved if the liquid remains perfectly colourless, or if it shows no more coloration than the blank test with distilled water. The brucine should be snow-white; if it is yellowish and dissolves in sulphuric acid with a brownish coloration, it should be rejected.

Other oxidising agents, such as chlorates, persulphates, free chlorine, etc., give similar reactions to nitric acid with sulphuric acid and brucine, but these substances do not occur in natural waters. A point of special interest is that nitrous acid gives no reaction with brucine and sulphuric acid if the sample of water is mixed with several times its volume of concentrated sulphuric acid, so that the nitrous acid is completely converted into nitrosyl sulphuric acid, and the brucine is only dissolved in the perfectly cooled liquid (Lunge, *cf.* p. 361); also, no reaction is produced by ferric salts. As is well known, natural waters often contain traces of ferric hydroxide in suspension, and nitric acid is often accompanied by nitrous acid. For these reasons the brucine reaction is far more suitable for the detection of nitric acid in natural waters than the otherwise extremely sensitive reaction with diphenylamine in sulphuric acid solution, as the latter reagent gives a blue coloration, not only with nitric acid, but also with nitrous acid and with ferric salts. If 1 volume of the water to be examined is mixed with only 0.5 volume of sulphuric acid, and brucine added to the perfectly cold liquid, the nitrous acid only reacts and not the nitric acid, if the quantity of the latter present is not great; further, if 2 volumes of concentrated sulphuric acid are mixed with the water, and the brucine is dissolved in the hot liquid, both acids react, almost immediately, giving a yellow coloration.

Ferrous salts interfere with both the diphenylamine and with the brucine test. If, for instance, the brucine sulphuric acid, which has been coloured pink with nitric acid, is treated with a drop of ferrous sulphate solution, the liquid is immediately decolorised; if, however, the colour has already changed to yellow, no appreciable change is produced by the ferrous sulphate. Any ferrous iron, therefore, which

is présent must be removed. This is effected by adding a few drops of sodium hydroxidè solution, free from nitrate, to the sample of water, and using the clear solution, obtained either by sedimentation or filtration, for the test. If the water is coloured, the organic substances must be removed by oxidation with potassium permanganate (*cf.* p. 750). In this case the nitrite will be oxidised to nitrate, and, after separate determination, must be deducted from the total nitrate obtained.

A large number of methods are available for the quantitative estimation of nitric acid, most of which depend either on the conversion of the nitric acid into easily determinable derivatives, such as nitric oxide or ammonia, or on the determination of the oxidising power of the nitric acid on certain substances, such as indigo; in addition, nitric acid can be determined colorimetrically by the brucine reaction, or by means of phenolsulphonic acid. A summary of the most important and satisfactory of these methods is given in the section on "Nitric Acid" (p. 309).

The most important of these methods in water analysis are the Schulze-Tiemann method, in which the nitric acid is reduced to nitric oxide, Ulsch's method, in which the nitric acid is reduced to ammonia, with iron, reduction to ammonia with the zinc-copper couple or with aluminium and sodium hydroxide, the Marx-Trommsdorff method of titration with indigo solution, and the approximate colorimetric estimations with brucine and with phenolsulphonic acid.

1. *The Schulze-Tiemann Method.* The nitric oxide obtained by the action of hydrochloric acid and ferrous chloride is collected in a graduated gas-measuring tube over a solution of sodium hydroxide, previously boiled, and the content of nitric acid deduced from the volume of gas obtained. This method is of general application, and gives sufficiently accurate results after some practice, although the values obtained are usually slightly too low. Organic admixtures or inorganic compounds, which may be present together with nitrates, do not affect the results. A detailed description of the method is given in the section on "Sewage" (p. 822).

2. *Ulsch's Method*<sup>1</sup> depends upon the reduction of the nitric acid to ammonia by means of ferrous hydrog. reductum and dilute sulphuric acid; the amount of nitric acid is deduced either from the amount of hydrogen used up or from the amount of ammonia formed. The method is described on pp. 311 to 315.

3. *Reduction by the Zinc-Copper Couple.*<sup>2</sup> The nitrogen present as nitrite is determined by reducing it to ammonia, and estimating the latter by Nesslerising (*cf.* p. 767). The method is simple, and according to Fowler, gives very accurate results.

<sup>1</sup> *Z. anal. Chem.*, 1891, 30, 175; 1892, 31, 392. *Z. angew. Chem.*, 1891, 4, 241.

<sup>2</sup> *Cf. Sewage Works Analyses*, by G. J. Fowler, pp. 68-70.

As is obvious, any nitrite present will also be reduced; the nitrogen combined as nitrite must therefore be separately estimated and deducted from the nitrogen present as nitrate.

The zinc-copper couple is prepared as follows:—A piece of zinc foil about 15 cm. long by 5 cm. wide is rolled into a cylinder about 1.5 cm. in diameter, then dipped for a moment into strong hydrochloric acid, to clean the surface of the metal, and afterwards well washed in water. The clean cylinder is transferred for a few moments to a 3 per cent. solution of copper sulphate until evenly coated with a black layer of copper. It is then again washed by gently immersing it in clean water so as not to dislodge the film of copper.

Before bringing the sample into contact with the couple, it is advisable to first drive off any free ammonia, if much is present, as otherwise the total amount of ammonia to be determined by Nesslerising may be inconveniently large, and the free ammonia must be deducted from the total ammonia present after reduction. Any error in the determination of free ammonia will therefore affect the nitrate determination.

One hundred c.c. of the water, or less if much nitrate is present, is diluted to 200 c.c. with distilled water free from nitrate and boiled down to about 50 c.c. This residual solution from which the free ammonia has been expelled is poured into a glass cylinder 15 cm. high by 2.5 cm. in diameter, and the zinc-copper couple, prepared as above, added. Thorough contact of the couple and the solution is thus ensured.

On slightly acidifying the solution with dilute acetic acid (1:2), an evolution of hydrogen occurs which reduces the nitrate to ammonia. For the reaction to be complete it should be left overnight, and as a further precaution, a known volume of the solution may be tested for nitrites in the morning; if present, it is evident that the reduction to ammonia is incomplete, and must be continued, but this is seldom, if ever, necessary. If the reduction is complete the solution is poured off from the couple into a litre flask, the couple washed free from adhering liquid and the washings added to the contents of the flask. Any free acid still remaining is neutralised with a little powdered sodium carbonate; tap-water is then added to make up the volume to about 500 c.c., and the ammonia distilled off and estimated as on p. 767.

From time to time a blank experiment should be made with the reagents used, the whole process being conducted as above, with the exception that distilled water is substituted for the sample. Any ammonia found in the blank experiment must be deducted from the total amount obtained from the sample.

4. *The Marx-Trommsdorff Method* depends upon the decolorisation of indigo by nitric acid in presence of concentrated sulphuric acid.

It can be rapidly carried out, and in spite of its inherent sources of error, can be recommended in all cases in which an approximate estimate of the amount of nitric acid in a water is sufficient. The following reagents are needed :—

1. *Dilute Indigo solution*.—One g. of purest, powdered indigo is evenly ground up in a small porcelain mortar with 5 to 10 c.c. of fuming sulphuric acid, and allowed to stand in a warm place for one to two hours; indigo-disulphonic acid is mainly formed together with a little mono-sulphonic acid. The liquid is then poured into about 300 c.c. of distilled water, mixed, and filtered. This concentrated indigo solution is diluted to ten times its volume for use; the solution must be kept in the dark. Best commercial indigo-carmin, the sodium salt of indigo-disulphonic acid, may be used instead of indigotin. In this case 2 g. of indigo-carmin are dissolved in 100 c.c. of dilute sulphuric acid, the solution diluted to about 300 c.c. and filtered; this concentrated solution is similarly diluted to ten times its volume before use.

2. *Purest Sulphuric acid*, free from nitrite and nitrate.

3. *Potassium nitrate solution*, of which 25 c.c. are exactly equivalent to 1 mg. of nitric anhydride (0.0749 g.  $\text{KNO}_3$  per litre).

The strength of the indigo solution must first be determined. For this purpose 25 c.c. of the potassium nitrate solution ( $=1 \text{ mg. N}_2\text{O}_5$ ) are placed in a small conical flask and 25 c.c. of concentrated sulphuric acid added with stirring; the temperature rises to about  $120^\circ$ . Indigo solution is then run in from a burette with a glass stopcock, the contents of the flask being well shaken, until the colour of the solution changes from yellow to a permanent green. Towards the end of the titration, when the green colouration, produced as the indigo solution enters, changes more and more slowly to yellow, the solution must be added in small quantities at a time, and finally drop by drop, in order not to miss the final change. The quantity of indigo solution used is then noted.

After this preliminary titration, a second estimation is made in which the total amount of indigo solution used in the first trial is added all at once and without shaking the flask; the whole is then shaken up until the liquid turns yellow, and further indigo solution added drop by drop till a pale greenish coloration results. It is possible, in this way, to work so quickly that the temperature of the solution does not sink below  $100^\circ$ . This second experiment shows the amount of indigo solution which corresponds to 1 mg.  $\text{N}_2\text{O}_5$ ; this should require from 8 to 10 c.c. of indigo solution (Sendtner).

The determination of the nitric acid in water is carried out in exactly the same manner as the titration of the indigo solution. For the first experiment 25 c.c. of the water are taken, 25 c.c. of sulphuric acid added, and the indigo solution run in, with constant shaking of the

flask, in a rapid sequence of drops, until the greenish shade is obtained. For the second titration, almost the total amount of indigo solution used in the first titration is added at once, and the operation continued as described above. After a little practice a third titration will agree with the second. The titration must be repeated a few times, as it is difficult at first to work sufficiently rapidly to prevent the temperature of the liquid sinking too low, with a water of which the content of nitric acid is unknown.

The results are calculated as follows:—If 25 c.c. of the water take 6 c.c. of indigo solution, and 9 c.c. of the indigo solution are equivalent to 1 mg.  $\text{N}_2\text{O}_5$ , then the 25 c.c. of the water contain  $\frac{6}{9} = 0.67$  mg.  $\text{N}_2\text{O}_5$ , and 1 litre of the water contains  $40 \times 0.67 = 26.8$  mg.  $\text{N}_2\text{O}_5$ .

If the content of nitric acid is more than 1 mg., or at the most 1.5 mg.  $\text{N}_2\text{O}_5$  per 25 c.c. of the sample—that is, if the first experiment requires more than 10 c.c. of indigo solution—it is necessary, in order to obtain accurate results, to dilute the water accordingly and to take the coefficient of dilution into account in calculating the result. Waters containing very little nitric acid must first be concentrated by evaporation.

This method of estimating the nitric acid is very quick, but the results are only approximate; much depends on practice and on rapidity in manipulation. The presence of considerable quantities of easily oxidisable organic substances decreases the accuracy, as these are oxidised by part of the nitric acid which would otherwise decolorise the indigo. According to Trommsdorff, the organic matter should first be removed by oxidation with potassium permanganate. To effect this, 100 c.c. of the water are acidified with about 1 c.c. of concentrated sulphuric acid in a beaker and a few drops of potassium permanganate solution added; the beaker is heated on the water-bath for ten to fifteen minutes, and oxalic acid solution added to the pink solution until it is just decolorised. After cooling, the liquid is diluted to 100 c.c., and the nitric acid determined as described.

Should the water contain considerable quantities of nitrous acid, it is best similarly to oxidise it with potassium permanganate to nitric acid, and to deduct the amount of nitric acid thus formed from the result of the final titration. The nitrous acid is determined in a separate sample of the water by the method described on p. 759.

5. *Colorimetric determination with Brucine.* The approximate amount of nitric acid can be determined colorimetrically by means of the reaction with brucine and sulphuric acid.<sup>1</sup> The method is most suitable for the analysis of waters containing little nitric acid and which are not too much contaminated with organic matter. It can accordingly

<sup>1</sup> Cf. *Chem. Zeit.*, 1899, 23, 454; and 1901, 25, 586.

be recommended for the analysis of drinking waters. The simplest manner of carrying out the determination is as follows:—

Two small flasks of about 50 c.c. capacity are taken, into one of which 10 c.c. of the water under examination are poured and into the other 10 c.c. of distilled water. So much pure brucine as will cover the point of a knife and a few drops of sulphuric acid are added to the contents of each flask, and after the brucine is dissolved 20 c.c. of concentrated sulphuric acid are added to each. The sulphuric acid is poured slowly down the side of the flask, in order to avoid ebullition of the liquid and loss of nitric acid. The water containing nitrate is coloured yellow, whereas the blank does not change colour at all, or becomes very faintly coloured if the sulphuric acid contains traces of nitric acid. Potassium nitrate solution is then added from a narrow burette to the distilled water solution whilst it is still hot, and the liquid shaken after addition of each drop until the colour of the two solutions is equal. Each c.c. of the potassium nitrate solution corresponds to 0.1 mg.  $N_2O_5 = 0.1872$  g.  $KNO_3$  per litre.

If the addition of the nitrate solution is not made sufficiently quickly the liquid in the comparison flask cools down too much, with the result that the red coloration with the brucine only changes slowly to yellow; in this case it is advisable to heat the liquid over the free flame for a short time. If the sample contains nitrous acid the amount present is calculated to nitric acid (factor = 1.42) and deducted from the total found.

The most satisfactory results are obtained if the amount of nitric acid present is from 2 to 30 mg. per litre; if the water contains much nitrate it should therefore be diluted accordingly, and if less than the above minimum it should be concentrated by evaporation. Any considerable quantity of organic matter present must first be destroyed by permanganate as in the case of the indigo method (p. 756); the disturbing effect of ferrous iron is similarly overcome.

If it is desired to express the result in terms of the nitric acid radical ( $NO_3$ ) the amount of nitric anhydride ( $N_2O_5$ ) found must be multiplied by 1.15.

The method may be improved by the use of special cylindrical, long-necked glass bottles of about 50 c.c. capacity, made from thin-walled glass tubing of about 3 cm. diameter, instead of the ordinary flasks. The bottles have two marks indicating volumes of 10 c.c. and 30 c.c. respectively.<sup>1</sup> In order to compare the colour of the two liquids as accurately as possible, the bottles are held over a sheet of milk-glass and compared from above, using a screen of black paper. As the columns of liquid are longer in this case than when flasks are used, the water must be diluted if it contains more than 10 mg. of nitric acid per litre.

<sup>1</sup> These bottles can be obtained from Dr Karl Kiss, Glastechnisches Institute, Budapest.

The accuracy of the result may be controlled by adding potassium nitrate solution to distilled water until it contains the quantity of nitric acid found in the sample under examination, and then comparing the coloration obtained on addition of the brucine and sulphuric acid; both liquids should acquire the same depth of colour; both can then be diluted to 100 c.c. and the colorations again compared.

6. *Colorimetric determination with Phenolsulphonic Acid.* The following description of this method is taken from the Report of the American Committee.<sup>1</sup>

*Reagents.*—1. *Phenolsulphonic acid.* Mix 30 g. of synthetic phenol with 370 g. of concentrated sulphuric acid in a round-bottomed flask; put the flask in a water-bath and support it in such a way that it shall be completely immersed in the water. Heat for six hours.

2. *Ammonium hydroxide solution* diluted with distilled water (1 : 1). Potassium hydroxide may be used.

3. *Standard Potassium nitrate solution.* Dissolve 0.72 g. of pure recrystallised potassium nitrate in 1 litre of distilled water. Evaporate cautiously 10 c.c. of this strong solution on the water-bath; moisten the residue quickly and thoroughly with 2 c.c. of phenolsulphonic acid, and dilute to 1 litre for the standard solution, 1 c.c. of which equals 0.00001 g. of nitrogen.

*Method of Determination.* Evaporate 20 c.c. or less of the sample in a small porcelain evaporating dish on the water-bath, removing it from the bath just before it has come to dryness; let the last few drops evaporate at room temperature in a place protected from dust. When the sample is suspected to contain a large amount of nitrate, evaporate less than 20 c.c.; if only a little, evaporate a larger volume.

If the sample has a high colour, decolorise it before evaporating, by means of washed aluminum hydroxide.

Add 1 c.c. of phenolsulphonic acid and rub this quickly and thoroughly over the residue with a glass rod, and then about 10 c.c. of distilled water, and stir with a glass rod until mixed; add next enough ammonium hydroxide solution (or potassium hydroxide, if the operation must of necessity be carried on in a room where ammonia distillations are made) to render the liquid alkaline, transfer the liquid to a 100 c.c. Nessler tube, and fill the tube to the 100 c.c. mark with distilled water.

If nitrates are present a yellow colour will be formed; this may be compared with permanent standards made for the purpose, and which keep satisfactorily for several weeks. The series of standards for comparison is made by putting the following quantities of the standard nitrate solution into 100 c.c. tubes and making up to the

<sup>1</sup> *Loc. cit.*, p. 40.

100 c.c. mark with distilled water, and then adding 5 c.c. of strong ammonia to the contents of each tube:—

Volume of dilute Standard Solution added, in c.c.	Weight of Nitrogen in mg.	Volume of dilute Standard Solution added, in c.c.	Weight of Nitrogen in mg.
0	0.000	15.0	0.015
1.0	0.001	20.0	0.020
3.0	0.003	25.0	0.025
5.0	0.005	30.0	0.030
7.0	0.007	35.0	0.035
10.0	0.010	40.0	0.040

Compare the sample treated as above described with the standards by looking down vertically through the tubes at a white surface, so placed in front of a window, that it will reflect the light upwards through them.

The figure obtained by this comparison divided by the number of c.c. of the sample which were evaporated gives the parts per million of nitrogen in the form of nitrate.

### Nitrous Acid.

Nitrous acid is detected qualitatively by adding a few drops of potassium iodide solution and 1 c.c. of starch solution to about 50 c.c. of the water, placed in a cylinder of colourless glass, and then acidifying the liquid with a few drops of dilute sulphuric acid. Iodine is liberated in presence of nitrous acid, and gives a blue coloration, the intensity of which varies according to the amount present. Direct sunlight should be avoided in making the test; the reaction is also only decisive if the blue coloration takes place immediately, or at latest within five minutes. Mistakes are best avoided by carrying out a parallel test with 50 c.c. of pure distilled water. The reaction is delicate; 0.1 mg. of nitrous acid per litre of water gives a distinct blue coloration. With small quantities of nitrous acid the presence of considerable quantities of organic matter may prevent or considerably retard the reaction; it has, however, been shown by Preusse and Tiemann that the reduction of nitrates in presence of sulphuric acid and organic matter, which Kammerer<sup>1</sup> regarded as likely to occur, does not take place. If iron is present in the water it must be removed, as ferric salts liberate iodine from solutions of metallic iodides (*cf.* p. 761).

Tiemann and Preusse have applied the metaphenylenediamine reaction discovered by Griess<sup>2</sup> to the detection and quantitative estimation of nitrous acid in water; triaminoazobenzene (Bismarck brown), a

<sup>1</sup> *Z. anal. Chem.*, 1873, 12, 377.

<sup>2</sup> *Ber.*, 1878, 11, 624.



substance of pronounced colour, is formed. The reaction is extremely sharp; with practice the coloration produced by 0.03 mg. of  $N_2O_3$  per litre can be recognised after an interval of about ten minutes. The reagent is prepared by dissolving 5 g. of metaphenylenediamine in water, adding dilute sulphuric acid at once until the liquid shows a distinctly acid reaction, and then diluting with distilled water to 1 litre. If the solution is coloured it must be decolorised by warming with ignited charcoal. It can be satisfactorily kept for months in a well-closed vessel.

To detect nitrous acid, 100 c.c. of the water are acidified with 1 c.c. of 30 per cent. sulphuric acid, in a cylinder of colourless glass, and 1 c.c. of the metaphenylenediamine solution added; a yellowish, golden-yellow, or yellowish-brown coloration is produced, according to the amount of nitrous acid present. The presence of organic matter does not affect the reaction. Aqueous solutions of metaphenylenediamine are very sensitive to the action of ferric compounds which colour them more or less yellow, but excess of sulphuric acid makes the diamine solution much more stable in this respect, so that the presence of small quantities of iron compounds does not essentially influence the reaction if the test is carried out as described above.

A subsequent method for detecting nitrous acid, also proposed by Griess,<sup>1</sup> but modified by Ilosvay<sup>2</sup> and by Lunge,<sup>3</sup> depends on the fact that an acetic acid solution of  $\alpha$ -naphthylamine and sulphanilic acid gives a distinct red coloration after a short time in presence of extremely small quantities of nitrous acid; the sulphanilic acid is converted by the nitrous acid into the corresponding diazo-compound, and the latter reacts with the  $\alpha$ -naphthylamine to form a red azo-dye. Pagnini<sup>4</sup> fixes the dyestuff on wool.

The reagent is prepared as follows:<sup>5</sup>—

(1) One g. of sulphanilic acid is dissolved in 14.7 g. of glacial acetic acid and 285 c.c. of water. This is best done by warming the sulphanilic acid with the glacial acetic, to which an equal bulk of water has been added. The remaining water should be added carefully, the mixture being warmed and stirred to keep the sulphanilic acid in solution.

(2) 0.2 g. of  $\alpha$ -naphthylamine is dissolved in 14.7 g. of glacial acetic acid and 325 c.c. of water. As in the case of the sulphanilic acid, the naphthylamine is best dissolved by warming, first with the acid, to which about twice its volume of water has been added, and afterwards adding the remainder of the water.

Equal volumes of the two solutions are mixed for use. The greater proportions of the solutions should, however, be kept separately, not

<sup>1</sup> *Ber.*, 1879, 12, 427.

<sup>3</sup> *Z. angew. Chem.*, 1889, 2, 666.

<sup>2</sup> *Bull. Soc. Chim.*, 1889 [3], 2, 317.

<sup>4</sup> *Chem. Centr.*, 1902, II., 770.

<sup>5</sup> Cf. Fowler, *Sewage Works Analyses*, p. 64.

more than two or three days' supply of the mixture being made up at once, as it tends to turn pink, owing to the development of nitrite in the solution from ammonia in the air.

To carry out the test, 20 c.c. of the water are mixed with 2 to 3 c.c. of the reagent and warmed to  $70^{\circ}$  to  $80^{\circ}$ . In presence of 0.001 mg. of nitrous acid per litre, a red coloration is observed within one minute. The test must be performed in filled stoppered vessels, as the nitrous acid present in the air is sufficient to show a reaction, the coloration from which travels down through the liquid from above, if its surface is exposed to the atmosphere for some time. According to observations by Tiemann the presence of nitric acid, ammonia, or of organic matter in the water exerts no appreciable effect on the reaction.

If nitrous acid is only present in traces its qualitative detection is usually sufficient. The quantitative estimation of minute quantities is effected colorimetrically by the methods of Trommsdorff,<sup>1</sup> Preusse and Tiemann,<sup>2</sup> or Lunge and Lwoff (p. 377); larger amounts of nitrous acid are determined iodometrically as follows:—

One hundred c.c. of the water are poured into a flask of 200 c.c. capacity, acidified with 20 c.c. of 10 per cent. hydrochloric acid, and 2 to 3 c.c. of starch solution added; about 5 g. of pure potassium hydrogen carbonate, in fair-sized crystals, are then added to the liquid. After gas has been evolved for about one minute, a small crystal (0.1 to 0.2 g.) of potassium iodide is added, and the separated iodine titrated after five minutes, with a very dilute sodium thiosulphate solution, of which 1 c.c. is preferably equivalent to 0.1 mg.  $N_2O_3$ . This solution is prepared either by diluting 26.3 c.c. of  $N/10$  sodium thiosulphate solution to 1000 c.c., or by dissolving 0.6532 g. of pure  $Na_2S_2O_3 \cdot 5H_2O$  in water and making up to 1 litre. The blue coloration of the liquid should not return within ten minutes of the completion of the reaction, otherwise the expulsion of the air or of the nitrogen monoxide was incomplete.

If the sample is turbid, or coloured yellow by iron-rust, it must first be filtered; it is also advantageous to remove ferrous iron. To remove all the iron with certainty, 1 to 2 c.c. of sodium hydroxide solution, free from nitrite, are added to 250 c.c. of the water, which is then allowed to stand in a completely filled stoppered flask for half a day; the water is then decanted or filtered off from the precipitate and the nitrous acid estimated.

Should the water contain considerable quantities of organic matter, this might combine with part of the liberated iodine, and thus give too low a value for the nitrous acid. To eliminate this source of error, 1 c.c. of iodine solution is added to 100 c.c. of the water under examination and to 100 c.c. of distilled water, and the iodine remaining in each

<sup>1</sup> *Z. anal. Chem.*, 1869, 8, 358; 1870, 9, 168.

<sup>2</sup> *Ber.*, 1878, 11, 627.

liquid titrated after five minutes; the difference corresponds to the correction to be added. This method can of course be adopted without modification in the case of water clarified by filtration or by sedimentation, but not if it has been clarified with the help of caustic alkali when it is strongly alkaline; in the latter case pure carbon dioxide is first passed through the liquid until it no longer turns phenolphthalein paper red; a large excess of carbon dioxide is to be avoided.

#### Phosphoric Acid.

To test for phosphoric acid qualitatively, from 500 to 1000 c.c. of the water are acidified with nitric acid and evaporated to dryness in a glass dish; the residue is repeatedly moistened with nitric acid and dried as thoroughly as possible. It is then extracted with a few drops of nitric acid and about 10 c.c. of distilled water, filtered, and the filtrate treated with 10 c.c. of ammonium molybdate solution, to which nitric acid has been carefully added until the precipitate formed in the first instance is just dissolved, and the whole warmed to 60° to 80°. In presence of phosphoric acid a yellow, heavy precipitate is formed, either at once or after standing for some time.

#### Carbonic Acid.

Natural waters usually contain but little free carbonic acid, the greater part being combined in the form of bicarbonates. As these latter compounds easily give up half of their carbon dioxide, a distinction is made between half- and completely-combined carbonic acid.

The presence of carbonic acid in water is detected by the white turbidity formed on addition of clear lime-water.

To test for free carbonic acid, 1 c.c. of distilled water is treated with one drop of phenolphthalein solution and one drop of very dilute sodium hydroxide solution, and from 5 to 20 c.c. of the water under examination then added to the rose-red liquid so obtained; if decolorisation takes place in a few minutes, free carbonic acid is present. Any acidity due to peat acids should be determined in a separate portion of the sample, after boiling off the carbonic acid.

To test for combined carbonic acid—that is, for bicarbonates—1 c.c. of distilled water is treated with a drop of methyl orange solution and a drop of very dilute hydrochloric acid and from 5 to 20 c.c. of the sample then added to the red solution obtained in this way; if the colour is changed to yellow, bicarbonates are present.

Trillich<sup>1</sup> gives the following volumetric method for the quantitative determination of free carbonic acid. A 100 c.c. measuring-flask, the mark of which is situated low down on the neck, is filled with the water

<sup>1</sup> *Die Münchener Hochquellenleitung aus dem Mangfalltale*, 1890, II., p. 63. *Anleitung zu hygienischen Untersuchungen*, Emmerich and Trillich, 3rd ed., p. 120.

to be examined by passing it through the flask for some time, so as to thoroughly replace the water which first enters, and which loses some carbon dioxide through contact with the air (*cf.* p. 776). The water above the mark is removed by means of a pipette, ten drops of alcoholic phenolphthalein solution added, followed by  $N/10$  sodium carbonate solution, which is added drop by drop until the liquid has attained a pale rose colour which, after carefully inverting the stoppered flask once, remains permanent for five minutes. Each c.c. of sodium carbonate solution used corresponds to 1.11 c.c. or 2.2 mg.  $\text{CO}_2$ .

To obtain the total volume of combined carbonic acid, that is, the sum of the half-combined and completely-combined carbonic acid, in c.c. per litre of water, the number of c.c. of  $N/10$  hydrochloric acid used in the determination of the "Alkalinity" (p. 737) is multiplied by 22.3; multiplying by 44 gives the carbon dioxide in g. per litre of water.

The sum of the free and combined carbonic acid gives the total carbonic acid. The above methods enable the combined carbonic acid to be determined accurately, but the free carbonic acid only approximately; the value found for the total quantity of carbonic acid is accordingly also only approximate, but it is sufficiently correct to meet the requirements ordinarily demanded in an analysis of drinking water.

An exact determination of the total carbonic acid can be made either gas-volumetrically by the Lunge-Marchlewski method (p. 149), or by the following gravimetric method, in which it is expelled by hydrogen generated in a given volume of the water, and weighed after absorption.<sup>1</sup> The total carbon dioxide can also be determined by Adeney's method (p. 780).

The water is collected at the source of supply in the stoppered bottle *a* (Fig. 185) of 500 to 600 c.c. capacity, particular care being taken that no water which has been in contact with the atmosphere remains in the bottle (*cf.* p. 776). After filling the bottle to overflowing it is stoppered, and the stopper fastened down with a thin piece of sheet rubber. For the determination, the stopper is replaced by the cylinder *b* and 20 g. of granulated zinc added; it is preferable to put the zinc in the bottle before charging with the water, and allow for its volume; 20 g. zinc = 2.5 c.c. The zinc should be previously washed, first with dilute hydrochloric acid and then with water, to remove any adherent zinc carbonate. The dropping-funnel *c* is then placed in position on *b*, as shown, and a calcium chloride tube attached at *d*; the other end of the calcium chloride tube is connected with a weighed potassium hydroxide

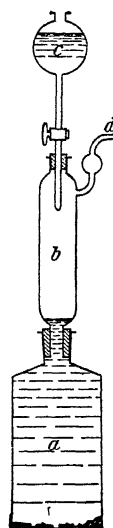


FIG. 185.

<sup>1</sup> L. W. Winkler, *Z. anal. Chem.*, 1903, 42, 735.

absorption apparatus. Fifty c.c. of 20 per cent. hydrochloric acid to which a drop of platinum chloride solution has been added are then gradually run into *a* through the dropping-funnel *c*, about an hour being taken for the addition. After the hydrogen has been generated for three hours the carbon dioxide is completely expelled. Finally, the hydrogen in the absorption apparatus is removed by passing a current of dry air free from carbon dioxide. The increase in weight of the absorption apparatus gives the weight of total carbon dioxide present in the water; 1 g.  $\text{CO}_2 = 506.4$  c.c.

### Calcium and Magnesium.

These substances are determined gravimetrically by the usual methods (*cf.* p. 405 *et seq.*).

The calcium can also be estimated volumetrically by Mohr's method, in which it is precipitated as calcium oxalate with an excess of titrated oxalic acid solution, and the excess of oxalic acid titrated back with potassium permanganate solution. The method is sufficiently exact for most hygienic purposes.

The magnesium can also be determined volumetrically. Of the various methods which have been proposed, that of Pfeifer<sup>1</sup> is carried out as follows:—

One hundred c.c. of the water are titrated, whilst boiling, with *N*/10 acid, with addition of alizarin, as in Wartha's method for the determination of alkalinity (p. 739). The water, which is then free from carbon dioxide, is rinsed with boiled distilled water into a 200 c.c. graduated flask and treated with a measured excess (25 to 50 c.c.) of lime-water; the flask is filled to 5 c.c. above the mark, closed with a rubber stopper, well shaken, cooled after a few minutes, and then the liquid poured on to a large pleated filter. The excess of calcium hydroxide is titrated back in 100 c.c. of the filtrate. The content of magnesium is calculated from the amount of calcium hydroxide used up; 1 c.c. of *N*/10 calcium hydroxide solution corresponds to 2.0 mg.  $\text{MgO}$ .

This method, if carried out with a little care, gives quite satisfactory results. It is important to use sufficient excess of the precipitant. The strength of the lime-water should be checked by a blank experiment, in order to eliminate experimental errors.

The total hardness of the water can be calculated (*cf.* p. 739) from the gravimetrically or volumetrically determined quantities of calcium and magnesium.

### Sodium and Potassium.

An ordinary water contains only minute quantities of sodium and potassium, the quantity of the former being almost always many times

<sup>1</sup> *Z. angew. Chem.*, 1902, 15, 199.

greater than that of the latter. These constituents of natural waters are generally of but little importance, either from a hygienic or technical standpoint; accordingly their direct estimation<sup>1</sup> is seldom undertaken.

If the calcium, magnesium, the total combined carbonic acid, sulphuric acid, nitric acid, and chlorine have been determined, the amount of the alkalis can be calculated. The result is certainly not exact, as is the case with most determinations by difference, but it is sufficiently correct for most purposes.

To arrive thus at the quantity of alkalis present, the quantities of bases and of acids found are divided by their equivalents and the quotients obtained for the bases and acids respectively added together. If the water contains alkalis the sum of the quotients from the bases will be smaller than the sum of those from the acids, and the difference multiplied by the equivalent weight of sodium oxide will give the amount of alkali in terms of  $\text{Na}_2\text{O}$ .

The following data of the water supplied to Budapest (April 1901) will serve as an example of the calculation. The subjoined table gives the analytical results, the equivalent weights of the bases and acids and their quotients:—

	In 1000 c.c. Water.	Equivalent Weights.	Quotients.	
Calcium oxide . . . .	77.8 mg.	$\frac{1}{2} \text{CaO} = 28.0$	2.78	} 4.00
Magnesium oxide . . . .	24.3 „	$\frac{1}{2} \text{MgO} = 20.0$	1.22	
Chlorine* . . . . .	3.7 „	$\text{Cl} = 35.5$	0.10	} 4.37
Sulphur trioxide . . . .	28.9 „	$\frac{1}{2} \text{SO}_3 = 40.0$	0.72	
Nitric anhydride . . . .	4.5 „	$\frac{1}{2} \text{N}_2\text{O}_5 = 54.0$	0.08	
Combined carbon dioxide . .	76.3 „	$\frac{1}{2} \text{CO}_2 = 22.0$	3.47	

\* It would be more correct, as dualistic formulæ are used, to express this as hydrochloric acid, and not as chlorine. But as the amount of chlorine is never expressed as hydrochloric acid in the results of water analyses, it is preferable to leave it as chlorine, especially as this has no influence on the value of the quotient.

The totals 4.00 and 4.37 differ by 0.37; this number multiplied by the equivalent weight of sodium oxide = 31, gives 11.5 mg.  $\text{Na}_2\text{O}$  per litre.

Ammonia and nitrous acid, etc., need only be taken into consideration if present in comparatively large quantity. Silica, though present in all waters, is of no consequence, as the silicic acid has no effect on methyl orange in the determination of the alkalinity.

#### Ammonia.

The potassium-mercury-iodide solution first recommended by J. Nessler, which consists of a solution of the double compound of potassium and mercuric iodides ( $\text{K}_2\text{HgI}_4$ ) in potassium or sodium hydroxide solution, forms an extremely sensitive reagent for the

<sup>1</sup> Cf. Thresh, *loc. cit.*, p. 242; also, Tiemann-Gärtner, *loc. cit.*, p. 108.

detection of ammonia. It gives a strong brownish-yellow coloration with extremely dilute ammonia solutions; the reaction is so sensitive that 0.05 mg. of ammonia can be detected in 1 litre of water. As, however, most natural waters contain considerable quantities of calcium and magnesium salts, a precipitate consisting of calcium carbonate and magnesium hydroxide is formed on addition of this reagent, which exercises a very disturbing effect in testing for very small quantities of ammonia. In order, therefore, to test for ammonia in natural waters it is necessary either to first remove the calcium and magnesium compounds by means of sodium hydroxide solution or to prevent their precipitation by the use of Rochelle salt; the latter procedure is certainly the simpler.

*Nessler's Reagent* as used for the detection and colorimetric estimation of ammonia is made up as follows:<sup>1</sup>—

62.5 g. of potassium iodide are dissolved in about 250 c.c. of distilled water, 10 c.c. of this solution are set aside, and into the remainder is carefully run a cold saturated solution of mercuric chloride. A brilliant red precipitate of mercuric iodide is formed, which at first quickly redissolves on shaking. The addition is continued till a permanent precipitate is obtained. This is redissolved by the potassium iodide held in reserve, and more mercuric chloride is added, drop by drop, until, after stirring, a red opalescence remains. One hundred and fifty g. of potassium hydroxide, dissolved in distilled water and allowed to cool are then added gradually, with continued shaking, to the opalescent solution. The whole is made up to 1 litre, allowed to settle, and the clear liquid decanted into a bottle.

The Nessler solution improves on keeping, and should therefore be made up some time before it is required for use. Special attention must be given to the end-point of the addition of the mercuric chloride to the iodide solution. If the potassium iodide be in excess, the reagent will not be delicate, and the coloration with ammonia will be a long time in reaching its full intensity. On the other hand, the addition of an excess of mercuric chloride will give an excess of mercuric iodide, which will dissolve when the potassium hydroxide is added, and the reagent will be exceedingly delicate and the full coloration will be obtained rapidly. The solution is liable, after the ammonia tubes have stood for about ten minutes, or even less, to become turbid and deposit a red crystalline precipitate, so that, whilst maximum delicacy is required, this turbidity is to be avoided. Practice is the only guide to making up a good Nessler solution: 1 c.c. of the solution should give a coloration with 0.008 mg.  $\text{NH}_3$  = 0.8 c.c.  $\text{N}/100$  ammonium chloride solution in 50 c.c. of pure water.

<sup>1</sup> Cf. Fowler, *Sewage Works Analyses*, p. 41; Wanklyn and Chapman, *Water Analysis*, 8th edition, 1891, p. 33.

*Rochelle Salt solution.* Fifty g. of crystallised Rochelle salt are dissolved in 100 c.c. of warm water, and 5 c.c. of Nessler's reagent added to the filtered solution in order to prevent mould-formation. Also, the solution should be kept in the dark. As commercial Rochelle salt almost always contain traces of ammonia, the liquid is yellowish at first, but becomes colourless on standing for from two to three days.

If it is necessary to filter the above Rochelle salt solution or the Nessler reagent itself, this is best done through a small plug of cotton-wool, rejecting the first portions of the filtrate.

For the detection of ammonia, 50 c.c. of the water to be examined are treated with 1 c.c. of the Rochelle salt solution and 1 c.c. of Nessler's reagent in a cylinder of colourless glass, and the colour of the liquid then observed by looking down through it obliquely on to a sheet of white paper placed below. If the water was originally colourless, a yellow or brownish-yellow tint is produced in presence of the smallest traces of ammonia.

The quantitative colorimetric estimation<sup>1</sup> is carried out as follows:—

Two glass-stoppered bottles each of about 150 c.c. capacity are required; cut-glass bottles are the most suitable, as they permit of the clearest observation of the colour. Glass cylinders about 4 cm. wide and 20 cm. high may also be used. One hundred c.c. of the water to be examined are placed in one of the bottles and the same quantity of ordinary water free from ammonia, or of distilled water, in the second; to each is then added 2 to 3 c.c. of Rochelle salt solution, followed, drop by drop, by the same quantity of Nessler's reagent, with stirring. A standard ammonium chloride solution, of which each c.c. is equivalent to 0.1 mg.  $\text{NH}_3$ , is then added, drop by drop, from a narrow burette, with shaking, to the contents of the bottle containing the ammonia-free water, until the colour of the two liquids is identical. The number of c.c. of ammonium chloride solution used gives the content of ammonia in the water under examination, in mg. per litre.

The ammonium chloride solution used for the estimation is prepared by dissolving 0.315 g. pure dry ammonium chloride in water and making up to 1 litre.

More exact results may be obtained by preparing a set of standard tubes either from Nessler's reagent with varying quantities of standard ammonium chloride solution, or from permanent standards made by mixing solutions of platinum and cobalt salts.<sup>2</sup>

The ammonia is then determined by adding 2 c.c. of Nessler's reagent to 50 c.c. of the sample and comparing the coloration with an equal volume of the standard mixture. It is important that the temperature of the sample and of the standard should be as nearly as possible the same.

<sup>1</sup> Cf. J. W. Winkler, *Chem. Zeit.*, 1899, 23, 454 and 541; 1901, 25, 586.

<sup>2</sup> Cf. Report of American Committee on Water Analysis, *loc. cit.*, p. 33.



The reagents (Nessler solution and Rochelle salt) cannot be kept ready mixed, because even after standing for one day crystalline mercurous iodide begins to separate in golden yellow scales resembling lead iodide, the quantity of which steadily increases; the reagent is then no longer suitable for the colorimetric estimation of ammonia, as it gives rise, not only to a coloration, but also to a turbidity. The best plan is to mix equal volumes of the two reagents as required, and to use 5 c.c. of the mixture for each experiment; this mixture is referred to as the "mixed reagent." The 5 c.c. of mixed reagent should be added to the 100 c.c. of water drop by drop, not all at once, as in the latter case a lemon-yellow coloration is often obtained instead of a brownish-yellow, which is prejudicial to the colorimetric comparison. Should the use of the mixed reagent cause a precipitation of mercuric iodide, which is usually due to the use of freshly prepared Nessler's reagent, 0.1 to 0.2 g. of potassium iodide are dissolved in 50 c.c. of the latter; a larger addition of potassium iodide diminishes the sensitiveness of the test.

Natural water is more suitable for comparison than distilled water, as the latter is usually less easily obtained free from ammonia. According to Winkler, the distilled water of laboratories often contains ammonia, which is only exceptionally derived directly from the air, being more probably due to the action of bacteria.

If the water under examination is turbid it must be filtered; it is advisable, in this case, to use a small filter paper and to reject the first 100 to 200 c.c. of the filtrate, which may have absorbed ammonia from the paper. If the water is very hard the mixed reagent causes a precipitate of the tartrates of the alkaline earths; in this case 100 c.c. of the water must first be mixed with 5 c.c. of the Rochelle salt solution and then with the mixed reagent.

The colorimetric determination cannot, of course, be made without preliminary treatment if the sample is coloured. It is sometimes possible to obtain a colourless liquid by adding to 500 c.c. of the water 1 c.c. of sodium hydroxide solution and an equal quantity of sodium carbonate solution, as the precipitate which is thus formed may carry down the coloured ingredients. If this method of decolorisation fails, that proposed by Miller<sup>1</sup> should be used, according to which the ammonia is distilled off, after addition of sodium carbonate, either with or without previous dilution, and determined colorimetrically in the distillate with Nessler's reagent. Special care must be taken in this case to be sure that the apparatus used is perfectly clean. The water under examination must fill at least two-thirds of the retort used for the distillation, and not more than two-fifths of the original volume of the water is distilled over. Emmerling<sup>2</sup> recommends that, in

<sup>1</sup> *J. Chem. Soc.*, 1849-50, 3, 117.

<sup>2</sup> *Ber.*, 1902, 35, 2291.

presence of albumen, the water should always be distilled for the determination of ammonia, as the direct determination in such cases is always inexact.

Should larger quantities of ammonia be present, which very rarely occur, however, in the case of an ordinary water supply, the sample may be distilled with sodium carbonate and the liberated ammonia determined in the distillate either alkalimetrically or by precipitation as ammonium platinichloride, with subsequent ignition and weighing of the residual platinum.<sup>1</sup>

### Albuminoid and Proteid Ammonia.

The nitrogenous organic substances which contaminate natural waters are of varying origin. Urea, hippuric acid, and uric acid may be introduced from human urine, or from that of carnivorous or vegetarian animals; leucine, tyrosine, aspartic acid, glutaminic acid, indole, skatole, etc., from excrements or from decay of albumins of either vegetable or of animal origin. Some idea of the amount of nitrogenous organic matter is obtained by the determination of the so-called *Albuminoid Ammonia*.<sup>2</sup> This is done by distilling a measured sample of the water with a strongly alkaline potassium manganate solution and estimating the amount of ammonia in the distillate. An indication may also be obtained of the amount of nitrogenous organic impurities, in solution and suspension in water, in a simpler manner, by oxidising with potassium persulphate in acid solution, and then determining the amount of ammonia formed colorimetrically in the liquid, thus avoiding a distillation. This is known as the determination of the *Proteid Ammonia*.<sup>3</sup> It is important to recognise that these determinations do not permit of the calculation of the absolute amount of nitrogenous organic matter present; the results obtained serve only as a guide to the proportions of these substances.

**Albuminoid Ammonia.**—The determination of albuminoid ammonia is conveniently combined with the estimation of the inorganic ammonia (free ammonia) present as such in the water. Miller's distillation method is employed for the determination (p. 768). In addition to the reagents already described for the determination of free ammonia, an alkaline potassium manganate solution is required; this is prepared as follows:—

One hundred g. of pure, commercial potassium hydroxide and 4 g. of crystallised potassium permanganate are dissolved in 500 c.c. of distilled water, and the solution boiled vigorously for fifteen minutes

<sup>1</sup> Cf. Tiemann-Gärtner, *loc. cit.*, p. 125.

<sup>2</sup> Cf. *Water Analysis*, by J. A. Wanklyn and E. T. Chapman, *loc. cit.*, p. 28; also, Tiemann-Gärtner, *loc. cit.*, p. 263.

<sup>3</sup> L. W. Winkler, *Z. anal. Chem.*, 1902, 42, 290.

in a large conical flask. Any traces of ammonia or of nitrogenous organic matter are thus expelled or destroyed. The concentrated liquid is then allowed to cool in a place free from ammonia, diluted with water to 500 c.c. and kept in a bottle provided with a well-ground glass stopper.

The determination is carried out in a tubulated retort of rather more than 1 litre capacity, the tubulure of which is provided with a ground-glass stopper. It is so connected with a condenser that the neck of the retort points somewhat obliquely upwards, and the condenser obliquely downwards; the neck of the retort is bent downwards at an obtuse angle at the end, and is drawn out so that it has the same diameter as the inner tube of the condenser, with which it is connected by a piece of boiled-out, black rubber tubing, in such a way that glass touches glass, and the steam accordingly comes into contact with the rubber as little as possible. Five hundred c.c. of the water under investigation are poured into the retort through the tubulure. Should the sample be acid, a little freshly ignited sodium carbonate must be added, in order to liberate the free ammonia, but this addition is usually unnecessary, as an ordinary water supply generally contains alkaline earth carbonates. The liquid is then distilled as quickly as possible, by heating the retort, at first carefully, with the naked flame of a triple burner, or in a suitable Babo funnel. The distillate is collected in two fractions, each of 100 c.c., in large Nessler glasses, and the distillation momentarily stopped when the second glass is full. The two glasses contain the whole of the free ammonia in the 500 c.c. of water, which is determined colorimetrically with Nessler's reagent.

After allowing to cool for a short time, the stopper of the retort is removed, and 50 c.c. of the strongly alkaline potassium manganate solution poured into the liquid, with gentle shaking, through a carefully cleaned glass funnel. The retort is then closed and the distillation resumed, two further fractions of 100 c.c. each being collected. This distillate contains the ammonia formed from the nitrogenous organic compounds, and is also colorimetrically estimated with Nessler's reagent.

**Proteid Ammonia.**—The following solutions are required for the determination of proteid ammonia in natural water:<sup>1</sup>—

1. *Potassium Persulphate solution.* Commercial potassium persulphate usually contains considerable quantities of the ammonium salt, and must therefore be purified. For this purpose 15 g. of the salt are powdered and dissolved in 100 c.c. of water at 50° to 60°, with addition of 1.5 g. of potassium hydroxide. The solution is filtered through a small plug of cotton wool, and allowed to stand in a cool place for a few hours. The crystals which separate are collected, washed with

<sup>1</sup> Cf. L. W. Winkler, *Z. anal. Chem.*, 1902, 42, 295.

cold water, and dried at the ordinary temperature. For use, 1 g. of the pure, powdered persulphate is dissolved in 100 c.c. of water. The solution does not keep long, and large quantities should, therefore, not be made up. The fresh solution is neutral, and gives no turbidity with barium chloride; a decomposed solution contains potassium hydrogen sulphate, gives an acid reaction, and is precipitated by barium chloride.

2. *Approximately N/5 Sulphuric Acid.* Six c.c. of pure concentrated sulphuric acid are diluted with water to 1 litre.

The reagents used for the determination of the liberated ammonia are the same as those required for the estimation of free ammonia.

The determination of proteid ammonia is carried out as follows:—A flask of about 200 c.c. capacity is first rinsed out with the water to be examined, and 100 c.c. of the sample then introduced; 5 c.c. of N/5 sulphuric acid, and 5 c.c. of the potassium persulphate solution are then added. The liquid should then be acid; if it is not, 5 c.c. more of the sulphuric acid are added. The flask is placed in a water-bath, in which the water is boiling vigorously, so that the whole of the lower portion of the flask is exposed to the steam, and the neck covered with a small beaker to prevent any appreciable loss by evaporation. After remaining on the water-bath for fifteen minutes, the flask is removed and the contents cooled completely by running water. The liquid is then poured into a cut glass bottle of about 150 c.c. capacity, or into a Nessler cylinder, and 5 c.c. of the "mixed" Nessler reagent (p. 768) added drop by drop. A separate 100 c.c. of the sample is also poured into a similar bottle or cylinder, and treated with 5 or 10 c.c. of N/5 sulphuric acid, 5 c.c. of the mixed Nessler reagent added drop by drop, and 5 c.c. of the potassium persulphate solution. The latter liquid will be slightly coloured, whilst the sample which has been heated will be darker according to the proportion of ammonia present. To determine the amount of proteid ammonia, ammonium chloride solution (1 c.c. = 0.1 mg.  $\text{NH}_3$ ) is added drop by drop to the less strongly coloured solution until the colorations are equal. The number of c.c. of ammonium chloride solution required to effect this gives the amount of proteid ammonia in mg. per litre of the original water.

The addition of sulphuric acid and persulphate solution to the solution used for comparison is important, as the reagents almost always contain traces of ammonia which would cause considerable error, which is avoided by the above method of procedure; also the proteid ammonia is determined independently of any free ammonia in the original water, as this is present in equal amount in both of the liquids under comparison.

The proteid ammonia determination is especially applicable to the analysis of drinking water.

The determination of albuminoid ammonia is more suitable in the

case of very turbid and coloured waters. The proteid ammonia determination can be carried out with waters which have been filtered, and if necessary diluted, but the values found refer only to the dissolved nitrogenous matter, and not to that present in suspension, as this is, of course, removed by the filtration.

The most minute amounts of substances of animal origin present in water can be detected with certainty by means of a proteid ammonia estimation; if, for instance, 10 c.c. of urine are added to 1 cubic metre of water, 0.1 mg. of proteid ammonia per litre will be found, even after a lapse of several weeks.

### Iron.

Iron is usually present in water, in solution as ferrous hydrogen carbonate; on standing in the air it is precipitated as insoluble brownish-red ferric hydroxide. In testing water for iron it is therefore necessary to note whether the iron has already separated in the form of flocculent particles; if this is the case, the yellowish-brown sediment must be collected on a filter, digested with hot, dilute hydrochloric acid, free from iron, and the solution tested for iron, after dilution, with potassium ferrocyanide or with ammonium thiocyanate.

If the iron is in solution it is best tested for qualitatively by adding a few drops of sulphuretted hydrogen water and 1 to 2 drops of ammonia to 100 c.c. of the sample; 0.1 mg. of ferrous iron in the 100 c.c. gives a distinct brown, and 0.01 mg. a perceptible coloration. To check that the reaction is not due to traces of lead or copper, acetic acid is added to the brown liquid to acid reaction; the coloration is destroyed if only due to iron, otherwise lead or copper is present. The reaction of ammonium sulphide with ferric iron is far less sensitive. A very dilute solution of a ferrous or ferric salt is coloured bluish-green by ammonium sulphide, in presence of much ammonia.

Iron is determined quantitatively either by titration or colorimetrically according as to whether it is present in appreciable quantity or only in traces; the latter method is usually preferable.

For the volumetric estimation from 500 to 1000 c.c. of the water are evaporated to dryness in a glass dish with a few c.c. of hydrochloric acid and 0.1 to 0.2 g. of potassium chlorate, which is added to destroy organic matter. If the iron has separated out through long standing, the entire contents of the sample bottle are used for the determination and the volume of the water found by subsequently calibrating the bottle. The bottle must be rinsed repeatedly with warm hydrochloric acid so as to completely remove any iron compounds adhering to the sides. The residue from the evaporation is warmed for some time on the water-bath with 20 c.c. of dilute sulphuric acid, the solution filtered from undissolved gypsum, silica, etc., and the residue washed with

10 to 20 c.c. of hot water. The iron in the filtrate and washings is then reduced with zinc or magnesium free from iron and titrated with  $N/100$  potassium permanganate solution (*cf.* p. 380).

To determine iron colorimetrically, either with potassium ferrocyanide or with ammonium thiocyanate, the ferrous iron must of course be first oxidised to the ferric condition; this is effected by means of hydrochloric acid and potassium chlorate as described above. The residue obtained on evaporation is dissolved in a few drops of hydrochloric acid, diluted with distilled water to 100 c.c., and the coloration produced on addition of potassium ferrocyanide or of ammonia thiocyanate compared with that obtained by adding progressively increasing quantities of ferric iron and the same volume of the reagent to 100 c.c. of distilled water<sup>1</sup> (*cf.* p. 381).

Whenever possible, the iron should be estimated at the source of supply in a freshly collected sample of the water. In this case the method can be simplified by omitting the oxidation and determining the ferrous iron colorimetrically with ammonium sulphide.<sup>2</sup> This method is therefore specially suitable for a continuous series of observations such as is required in testing a process for the removal of iron.

The solution employed as a standard for comparison is prepared by dissolving 0.7 g. of ferrous ammonium sulphate and 1 c.c. of dilute sulphuric acid in 1 litre of sulphuretted hydrogen water; 1 c.c. of this solution contains 0.1 mg. Fe. The solution must be kept in well-closed vessels, and should not be used after it ceases to smell of sulphuretted hydrogen; it is best to divide it up in small bottles, closed with sound corks and sealed with paraffin-wax. In this way the solution can be kept unchanged for years; a solution which has spoilt by standing can be regenerated by saturation with sulphuretted hydrogen.

For the determination, 100 c.c. of the water are treated with 5 c.c. of sulphuretted hydrogen solution, and 1 to 2 drops of ammonia in a colourless glass cylinder, about 4 cm. wide and 20 cm. high. One hundred c.c. of distilled water are similarly treated also with 5 c.c. of sulphuretted hydrogen solution and 1 to 2 drops of ammonia, and the standard ferrous ammonium sulphate solution then added drop by drop, with shaking, until the depth of colour of the two liquids is approximately equal; the comparison cannot be taken as correct at this stage, as the sample is coloured brown whilst the standard inclines to a bluish-black. To the latter, 2 to 3 drops of dilute hydrochloric acid are therefore added, followed, after decolorisation, by a few drops of aqueous ammonia, which bring back the coloration to the brown tint of the sample; a further quantity of the ferrous ammonium sulphate

<sup>1</sup> *Cf.* Tiemann-Gärtner, *loc. cit.*, p. 80.

<sup>2</sup> L. W. Winkler, *Z. anal. Chem.*, 1902, 41, 550.

solution is then added until the colorations are equal. Finally, both liquids are decolorised by adding a few drops of dilute hydrochloric acid and the colour regenerated with ammonia, when the two colorations should again be equal. The amount of iron present in mg. per litre of the original sample is equal to the number of c.c. of the ferrous ammonium sulphate solution used.

This method only gives accurate results if the water under examination contains from 0.3 to 1.5 mg. of ferrous iron per litre; if the quantity of iron is less than 0.3 mg. per litre the colorimetric comparison is made in higher and rather wider cylinders with 500 c.c. of the water, and if greater than 1.5 mg. per litre, a measured volume of the water, to which a few c.c. of sulphuretted hydrogen water have been added, and which is therefore deeply coloured, is correspondingly diluted for the comparison.

To carry out this determination in the laboratory the iron is kept in the ferrous condition by acidifying the water in the collecting vessel with a few drops of hydrochloric acid and adding 10 c.c. of 10 per cent. sulphuretted hydrogen water; no oxidation to ferric iron occurs so long as the water smells of sulphuretted hydrogen. In this case the colorimetric comparison is of course carried out with 110 c.c. instead of with 100 c.c. of water. If the sample also contains lead it is treated as above with hydrochloric acid and sulphuretted hydrogen solution, allowed to stand overnight, the water then decanted from the precipitated lead sulphide and sulphur, and estimated as above.

Should it be necessary to determine how much iron is present in solution and in suspension respectively, the water is treated with 50 c.c. of sulphuretted hydrogen solution per litre, without addition of acid, and filtered; the ferrous sulphide formed is at first in the colloidal condition and is not retained in perceptible amount by the filter paper. One hundred and five c.c. of the filtrate are then taken for the colorimetric estimation, which thus gives the dissolved iron; this deducted from the total iron gives the insoluble iron by difference.

The total iron may be determined by the above method, but in this case the ferric iron must first be reduced with sulphuretted hydrogen to ferrous iron. From 10 to 500 c.c. of the water, according to the amount of iron present, are evaporated to dryness in a glass dish with a few c.c. of hydrochloric acid and 0.1 g. of potassium chlorate. The residue is warmed on the water-bath for a few minutes with a few drops of hydrochloric acid and about 10 c.c. of water, and about 5 c.c. of sulphuretted hydrogen water added to the liquid whilst still warm. After cooling it is filtered through a small filter, and washed with distilled water until the volume of the filtrate is 100 c.c. The iron is then determined in the filtrate as described above. The filtrate is somewhat opalescent, owing to the presence of finely divided sulphur,

but, this is of no consequence, as on addition of the sulphuretted hydrogen water and ammonia the sulphur dissolves in the ammonium sulphide which is formed.

If the water is coloured this process need not be modified, as the coloured substances are destroyed by the chlorine which is generated.

### Lead.

Lead may be introduced into a water supply through the material of the mains and pipes; although the quantities thus dissolved are small, they are by no means indifferent from a hygienic standpoint. The lead is present in the water as dissolved lead hydrogen carbonate; on standing in the air, or on boiling, the lead is precipitated together with the calcium carbonate.

To test qualitatively for lead, 100 c.c. of the water are poured into a beaker, acidified with acetic acid, and treated with a few c.c. of sulphuretted hydrogen water; the liquid is coloured brownish-yellow even if the water only contains a few tenths of a mg. of lead per litre. The presence of iron does not interfere, as it does not react with hydrogen sulphide in acid solution.

If the water contains only 0.1 mg. or less lead per litre it must be concentrated by evaporation. G. Frerichs<sup>1</sup> has made the very important observation, that if water containing lead is filtered through pure cotton-wool the lead is completely retained and the water thus freed from lead. This property of cotton-wool can be utilised for the qualitative detection and for the quantitative estimation of even the smallest quantities of lead in water. For the detection of very small quantities of lead the following method may be adopted:—

A plug of cotton-wool weighing 0.5 to 1 g. is pressed into a glass funnel and moistened with distilled water so that it adheres to the funnel. About 1 litre of the water is then filtered through the cotton-wool. To redissolve the retained lead a mixture of 10 c.c. of distilled water and 1 c.c. of dilute acetic acid is heated to boiling and poured, one c.c. at a time, on to the cotton-wool; the acid liquid completely removes the lead, so that the filtrate gives a strong reaction with sulphuretted hydrogen water even if only traces of lead are present, as the lead is concentrated nearly a hundredfold by this method. In order to be certain that the reaction is not due to copper the process is repeated, but instead of adding sulphuretted hydrogen water to the acetic acid filtrate, an excess of ammonia is added. The solution is then warmed, filtered to remove any iron which may be present, and evaporated to dryness in a very small glass dish; the residue is dissolved in a drop of hydrochloric acid and a few drops of water, and tested for copper with potassium ferricyanide.

<sup>1</sup> *Apoth. Zeit.*, 1902, 884.



The quantitative estimation of lead is also based on the reaction with sulphuretted hydrogen, and is carried out colorimetrically. A lead solution containing 0.1 mg. lead per c.c. serves as a standard, and is prepared by dissolving 0.16 g. of dry powdered lead nitrate in distilled water and making up to 1 litre. Quantities of 0.5, 1.0, and 1.5 c.c., or of 1.5, 2.0, and 2.5 c.c. of this lead solution, according to the depth of colour observed in the qualitative test, are each diluted in colourless beakers with water free from lead up to 100 c.c., and acidified with 1 c.c. of acetic acid. One hundred c.c. of the sample are poured into a similar beaker, also acidified with 1 c.c. of acetic acid and 10 c.c. of sulphuretted hydrogen water then added to the contents of each beaker, and the colorations compared. If only traces of lead are present it is concentrated by Frerichs' method as described above. To secure accuracy one litre of the water is filtered several times successively through the cotton-wool. After dissolving the lead in hot water containing acetic acid, washing is continued with water free from lead until the volume of the liquid amounts to 100 c.c. The colorimetric determination is then carried out with this tenfold concentrated solution.

If the water is coloured it must be decolorised previous to the determination of lead. One hundred c.c. are acidified with a few drops of hydrochloric acid, a few c.c. of chlorine water added, and the liquid boiled in a conical flask until the excess of chlorine is expelled; ammonia is then added to the cold solution until it is just alkaline, the whole diluted to 100 c.c., 1 c.c. of dilute acetic acid added, and the colorimetric determination carried out as above.

### The Determination of Dissolved Gases.

Almost every natural water contains free carbon dioxide and air in solution. Ground water sometimes also contains small amounts of hydrogen sulphide. Methane only occurs in ordinary natural waters exceptionally and in small quantity; on the other hand, many artesian waters are supersaturated with methane, so that the gas issues with the water.

The gases in natural waters can only be correctly determined if the sample is collected directly in the vessel in which the estimation is to be made, and if care is taken that the water which first enters the collecting bottle, and has therefore been in contact with air, is completely removed. In the case of water from supply pipes, this is effected by passing the water into the bottle for some minutes through a narrow glass tube reaching to the bottom. To examine the water from a well provided with a pump, water is first pumped for ten minutes; the outlet pipe is then closed with a rubber stopper provided with a glass tube which also passes to the bottom of the collecting bottle. Water is then pumped through for at least five more minutes, so that a satisfactory

sample is obtained. In the case of running water the collecting bottle, provided with a rather wide, bent tube, is fastened to a pole and lowered into the water to the required depth (Fig. 186); a quarter of an hour should be allowed for the original contents of the bottle to be thoroughly renewed. The bottle is then lifted to the surface after the removal of the glass tube. To collect a sample of standing water, the bottle, which is fastened to a pole, is provided with a thin lead or ebonite tube to which a short glass tube is attached, and lowered to the necessary depth. The tube is then connected with a small hand-pump, and about ten times as much water as the capacity of the bottle pumped through. The most reliable plan is to fix a spring cap to the neck of the bottle, so that it is closed automatically after the removal of the tube. If possible, the gaseous contents should be determined at once; if this cannot be done, glass-stoppered bottles are used for collecting the sample. Care must be taken that no air-bubbles remain on closing the bottle; the stopper is covered with a piece of thin sheet rubber for transport.<sup>1</sup>

Glass bottles provided with glass stoppers and overlapping glass caps, both well ground, are also very suitable as collecting vessels.<sup>2</sup> After the bottle has been filled in the manner described above, the glass cap is also filled with the water and then placed in position.

A full account of the chief methods in use for sampling river waters is given by Schumacher.<sup>3</sup>

The determination of free carbon dioxide has already been described (p. 762); the following methods serve for the determination of the other dissolved gases, more particularly nitrogen, oxygen, methane, and hydrogen sulphide.

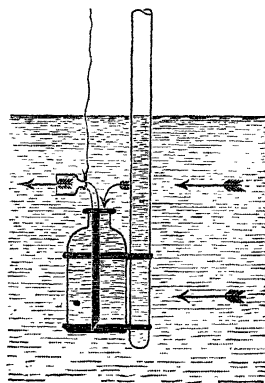


FIG. 186.

### Nitrogen, Oxygen, Methane.

The determination of dissolved oxygen and of atmospheric nitrogen (*i.e.*, nitrogen derived from air, containing argon, etc.) in natural waters is easily carried out by expelling the dissolved gases by carbon dioxide and collecting them over sodium hydroxide solution.<sup>4</sup> The amount of dissolved oxygen is most accurately determined iodometrically (p. 782). In gaseous mixtures expelled from water it is most

<sup>1</sup> Cf. L. W. Winkler, *Z. anal. Chem.*, 1901, 40, 532.

<sup>2</sup> Farnsteiner-Buttenberg-Korn, *Leitfaden für die chemische Untersuchung von Abwässern*, p. 34.

<sup>3</sup> *Gesundheits Ingenieur*, 1904, Nos. 26, 27, and 28. Published by R. Oldenbourg, Munich.

<sup>4</sup> L. W. Winkler, *Z. anal. Chem.*, 1901, 40, 523.

easily determined by absorption with alkaline pyrogallol solution. The oxygen and nitrogen dissolved in water are expelled by carbon dioxide in the following manner:—

Ten g. of coarse-grained calcite, freed from dust by sieving, are placed in a 500 c.c. flask or bottle (Fig. 187), the capacity of which has been determined up to the stopper. A little water, acidified with hydrochloric acid, is poured on to the calcite and poured off again, after gas has been generated for one to two minutes; the object of this is merely to moisten the calcite evenly. The water under examination is then passed through the flask, in a suitable manner, for a considerable time, so as to ensure a satisfactory replacement of the initial contents. The flask is completely filled with the sample, and 20 c.c. of fuming hydrochloric acid of sp. gr. 1.18 to 1.19 quickly added from a pipette; the acid is allowed to flow into the neck of the flask, not on to the bottom. The evolution of gas

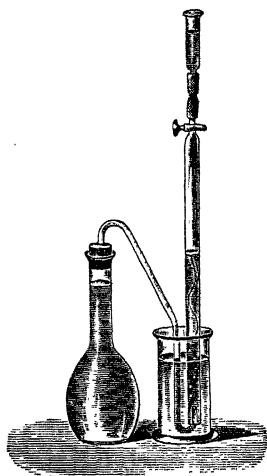


FIG. 187.

does not start immediately, so that there is time to insert the rubber stopper, which is fitted with a thick-walled gas delivery tube, into the neck of the flask, and to place the other end of the delivery tube under the measuring tube, which is filled with a 20 per cent. sodium hydroxide solution; this tube is about 40 c.m. long and 1 c.m. wide. The carbon dioxide, which is evolved in very small bubbles, carries the dissolved gases into the measuring tube. The operation is completed in fifteen to twenty minutes. To ensure the absorption of the carbon dioxide, the tap of the measuring tube is opened momentarily from time to time, and fresh sodium hydroxide solution admitted through the attached funnel.

The measuring tube is then transferred from the alkali solution by means of the small bottle hung on a piece of wire (Fig. 188), and placed first for a few minutes in a beaker containing distilled water, to allow the heavy liquid to diffuse out as far as possible, and then in a glass cylinder, provided with a thermometer and cardboard cover (Fig. 189); water is poured into the cylinder, so that it stands 1 to 2 mm. higher than the column of liquid in the measuring tube,

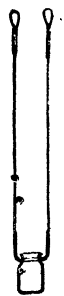


FIG. 188.

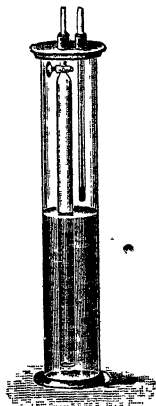


FIG. 189.

and the volume of gas, temperature, and pressure read, after allowing to stand for about twenty minutes.

The oxygen is determined in the mixture of oxygen and nitrogen thus obtained by the ordinary methods of gas analysis<sup>1</sup> (*cf.* p. 209).

The volume of air contained in the fuming hydrochloric acid used and the volume occupied by the calcite may be neglected in ordinary determinations. In the case of more exact measurements they must, however, be allowed for:—10 g. of calcite occupy a volume of 3.6 c.c.; from 1 litre of 38 per cent. hydrochloric acid, saturated with air at the ordinary temperature, 9.58 c.c. of nitrogen and 4.17 c.c. of oxygen were obtained on boiling, so that the correction to be deducted for 20 c.c. of hydrochloric acid is 0.192 c.c. of nitrogen and 0.083 c.c. of oxygen.

If the water contains considerable quantities of methane, the residual gas, after absorption of the oxygen, is inflammable. Small quantities of methane can only be detected by quantitative methods. For its estimation the gas from a separate 500 c.c. of the water is expelled with carbon dioxide as above, and collected in a small gas-holder filled with mercury containing 25 c.c. of 50 per cent. sodium hydroxide solution, to absorb the carbon dioxide. The gas thus obtained is then analysed by the usual methods (*cf.* p. 213).

*Adeney's Apparatus for the Extraction and Analysis of the Gases dissolved in Water.*<sup>2</sup> This is a very useful and applicable form of apparatus; it has been employed in a number of important researches made in connection with the work of the Royal Commission on Sewage Disposal.

The apparatus consists of a gas burette enclosed in a glass cylinder, a pressure tube, a laboratory vessel, and a laboratory flask with an intermediate condenser. The way in which these parts are fitted together and supported is shown in Fig. 190.

The upper end of the burette is closed by a Friedrich's two-way stopcock, by means of which communication can be opened or closed between it and the laboratory vessel, or laboratory flask, through the two branch tubes which lead from the upper side of the stopcock. The branch to the laboratory vessel is a capillary tube, that to the flask is of 2 or 3 mm. bore. The lower portion of the burette is contracted and passes through a hole cut in the centre of a rubber bung, which closes the lower end of the glass cylinder surrounding the burette. It is then bent at right angles and connected by rubber tubing with the similarly bent end of the pressure tube. The upper contracted portion of the burette is about 225 mm. long, and has a capacity of 15 c.c.; the wider

<sup>1</sup> *Cf.* L. W. Winkler, *Z. anal. Chem.*, 1901, 40, 529.

<sup>2</sup> *Trans. Royal Dublin Society*, New Series, 1895, Vol. V., Part XI. The editor is indebted to Dr Adeney for this description of his apparatus.

portion is about 410 mm. long, with a capacity of a little more than 250 c.c.; both portions are graduated, the former in one-tenth c.c., and the latter at intervals of 25 c.c. The pressure tube has a working length of 1000 mm., above the level of the lowest division of the burette. Its upper end is also closed by a Friedrich's stopcock. The supply of mercury to the burette and to the pressure tube is regulated by means of a reservoir, which can be moved vertically up and down at the back of the apparatus by a catgut line passing over the necessary pulleys to

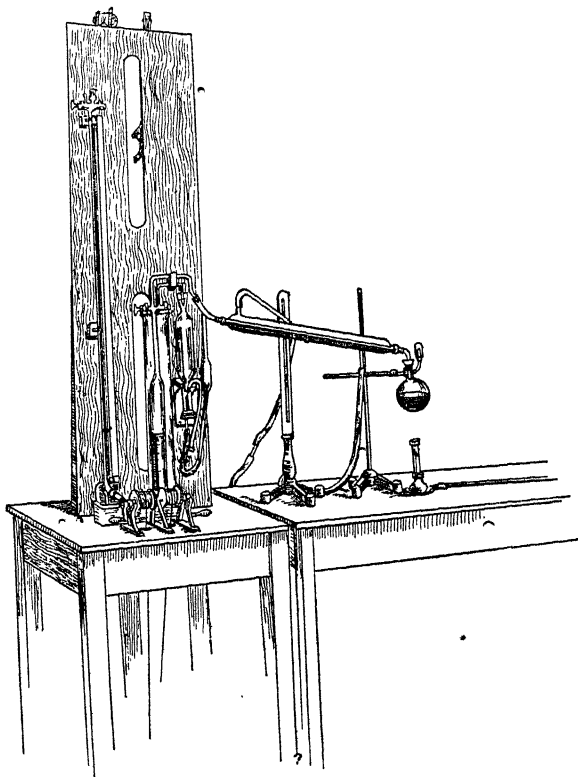


FIG. 190.

a windlass in front of the apparatus, as shown. The flexible tube from the reservoir is attached to a side branch fused to the lower portion of the pressure tube. The height of the mercury in the pressure tube is read by means of a millimetre scale etched on the unsilvered surface of a narrow slip of looking-glass, fixed at the back of, and close to, the pressure tube, at an angle so as to reflect the image of the tube through the portion of the glass bearing the scale.

The laboratory vessel differs in principle and shape from that used in Frankland's and Macleod's apparatus. Its shape is shown in the

figure; the lower contracted portion is 25 mm. in diameter, and 55 mm. long; it is furnished with a branch tube for connecting the vessel with a separate reservoir, which can be drawn up and down by a catgut line and a second windlass in a similar manner to that connected with the pressure tube. The middle portion is 160 mm. long, and the upper end has a funnel shape; it is 55 mm. long, and the diameter increases from 3 or 4 mm. to 20 mm. at the mouth. Two platinum wires are sealed in the sides of the vessel, for explosions. The funnel shape of the upper portion of the laboratory vessel enables it to be easily connected with, or disconnected from, the branch tube of the burette. The end of this tube is fitted with a rubber collar, and when the vessel is placed in position, the collar fits into the funnel and tightly closes it. The laboratory vessel is at the same time supported by a horseshoe-shaped shelf, as shown. If the space above the rubber collar be filled with mercury, a perfectly air-tight joint is obtained, and a vacuum can be maintained in the vessel, or explosions may be made in it without fear of loss. To disconnect the laboratory vessel, its lower end is drawn forward sufficiently to clear the shelf, and it is then lowered to detach it from the branch tube. By reversing these movements the laboratory vessel may again be placed in position. The lower end of the vessel is closed by a rubber cork, and in order to provide the means of introducing gaseous or liquid reagents into the vessel, a glass capillary tube about 100 mm. long is fitted through the cork; the outer end of this tube is closed by a piece of capillary rubber tubing and a small screw clamp.

The method of working the apparatus is as follows:—The burette, pressure tube, and laboratory vessel are filled with mercury. The laboratory flask, which has a capacity of about 1600 c.c., is fitted to the end of the condenser as shown in the figure, 50 c.c. of distilled water and generally a little sulphuric acid having been previously put into the flask. The water in the flask is then boiled, the air and steam escaping through the side tube in the neck of the flask. The boiling is continued for a few minutes, the burner then removed, and at the same time the side tube closed by a piece of rubber tubing and glass rod. The air still remaining in the flask is exhausted by working the burette and its reservoir as a Töpler pump. As air is drawn from the laboratory flask into the burette at each stroke of the reservoir, it is allowed to escape to the laboratory vessel. After the flask has been completely exhausted the vessel is disconnected from the branch tube, and a known volume of the water to be examined is drawn into the burette and then allowed to flow into the flask; the laboratory vessel is then replaced in position and re-connected with the branch tube. The water is boiled and the gases drawn into the burette and thence into the laboratory vessel for storage. After the gases have been completely extracted

they are measured and analysed, the absorptions (and explosions if necessary) being carried out in the laboratory vessel.

This apparatus has been found capable of yielding extremely accurate results both for extracting dissolved gases and for their analysis. By combining the principle of the Töpler pump with the burette, and by the employment of a closed laboratory vessel with a separate mercury reservoir, the difficulties of the older forms of apparatus for extracting and analysing dissolved gases are entirely overcome.

*L. W. Winkler's Iodometric Method*<sup>1</sup> is specially suitable if the dissolved oxygen only is to be determined in water. The method is based on the oxidation of manganous hydroxide to manganic hydroxide in presence of alkali by means of the oxygen dissolved in a measured quantity of the water; potassium iodide and hydrochloric acid are then added to the liquid, whereby the equivalent in iodine of the dissolved oxygen is liberated, which is titrated with sodium thiosulphate and calculated to oxygen.

The following solutions are required :—

1. *Manganous chloride solution.* Forty g. pure crystallised manganous chloride,  $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$ , are dissolved in 100 c.c. of water. The manganous chloride must be free from iron, and should separate at most only traces of iodine from an acidified solution of potassium iodide.

2. *Sodium hydroxide solution.* One part of pure sodium hydroxide, free from nitrite, is dissolved in 2 parts of water. About 10 per cent. of potassium iodide is dissolved in a portion of this solution for use; the mixture should not colour starch solution blue immediately after dilution and acidification with hydrochloric acid; also it should not contain much carbonate.

The estimations are carried out in thick-walled bottles of about 250 c.c. capacity, and provided with well-ground glass stoppers; the exact capacity must be known. The bottle is completely filled with the water by simply pouring it in, if the sample is saturated with air; if not, the water must be passed through the bottle until the initial contents have been fully replaced. The reagents are then introduced at once by means of 1 c.c. pipettes provided with long, narrow delivery tubes which are inserted nearly to the bottom of the bottle. One c.c. of the alkaline potassium iodide solution is first introduced, followed by 1 c.c. of the manganous chloride solution; the bottle is then closed, taking care that no air-bubbles adhere, which are easily excluded by first moistening the stopper by immersion in water. The contents of the bottle are then thoroughly mixed by shaking and turning it upside down. After a few minutes the flocculent precipitate settles and the liquid in the upper part of the bottle becomes almost clear; if this clear liquid is brownish in colour, instead of colourless, the shaking is

<sup>1</sup> *Ber.*, 1888, 21, 2843; 1889, 22, 1764.

gently repeated. If the bottle is shaken for an unnecessarily long time the precipitate loses its flocculent character and becomes powdery, and then only settles slowly. If time permits, it is best to let the precipitate settle completely; in order to keep out the air, the bottle is dipped, stopper downwards, into a small beaker filled with water, and then turned upright again with the beaker. (Fig. 191.) It is, however, usually sufficient to allow the bottle to stand for a few minutes. When the precipitate has settled so that the liquid in the upper part of the bottle is clear, the stopper is removed and about 5 c.c. of fuming hydrochloric acid added by a pipette with a long delivery tube previously moistened with water. The bottle is then again closed and the contents mixed; the precipitate quickly dissolves and a liquid coloured yellow by iodine is obtained; this is titrated with an  $N/100$  sodium thiosulphate solution in the usual manner; each c.c. of this corresponds to 0.055987 c.c. oxygen at  $0^\circ$  and 760 mm.

No correction is made in the method, as described, for the quantity of dissolved oxygen in the reagents, but as the total volume of the latter is approximately only 1 per cent. of the total liquid, the error from this source is practically negligible. For standard determinations air-free reagents must be used and the hydrochloric acid must be freed from all traces of air by treatment with carbon dioxide.<sup>1</sup>



FIG. 191.

As manganous carbonate is not oxidised by oxygen, a double quantity of sodium hydroxide solution, that is, 2 c.c., must be used in the case of waters containing considerable quantities of carbon dioxide.

Dissolved oxygen can be very accurately determined in pure natural waters by this method. If, however, the water contains considerable quantities of organic matter, this may combine with some of the iodine, so that less oxygen is found than is really present. To avoid this source of error, 100 c.c. of distilled water and 100 c.c. of the water to be examined are each treated with 10 c.c. of  $N/100$  iodine solution, and the amount of iodine remaining in each liquid titrated with  $N/100$  sodium thiosulphate solution after a few minutes. The difference in the amount of thiosulphate solution used in the two cases gives the value of the correction per 100 c.c. of the water.

The presence of nitrous acid in a water, even to the extent of 0.1 mg. per litre, interferes seriously with the reliability of the method. Nitrous acid liberates iodine from the acidified potassium iodide solution, but

<sup>1</sup> Cf. L. W. Winkler, *Ber.*, 1889, 22, 1764.



the quantity of iodine formed in this way is usually negligibly small; the serious interference with the reaction is caused by the nitric oxide formed from the nitrous acid, which acts as an oxygen carrier in much the same way as in the ordinary sulphuric acid process, causing a continuous absorption of oxygen from the air, during the titration. This source of error is easily avoided, however, by using a sodium hydroxide solution without the potassium iodide, for the determination of the oxygen; on addition of the hydrochloric acid, manganic chloride is formed, which is an energetic oxidising agent and immediately converts the nitrous into nitric acid. The potassium iodide is then added to the liquid, when it dissolves the suspended precipitate. The liberated iodine is then titrated with sodium thiosulphate solution. The manganic chloride, however, not only oxidises the nitrous acid, but also any organic matter present in the water; this occurs at the expense of the dissolved oxygen, and must accordingly be corrected for.

This modified process, which must always be adopted if more than 0.1 mg. of nitrous acid per litre is present, is carried out as follows:—

The sodium hydroxide solution prepared as above, but without the potassium iodide, is used, and double the quantity of hydrochloric acid (about 10 c.c.) is added after the precipitate has settled; otherwise the process is carried out as described above. After mixing, and subsequently waiting for two to three minutes, a small crystal of potassium iodide is added and the solution titrated. The manganic chloride solution required to correct for the presence of organic matter is prepared just before use, by adding 1 c.c. of the sodium hydroxide solution, followed by 5 to 10 drops of the manganous chloride solution, to 20 c.c. of distilled water; the mixture is allowed to stand for some minutes, with repeated shaking, so that plenty of manganic hydroxide may be formed. Sufficient fuming hydrochloric acid to dissolve the precipitate is then added, and the brown solution finally diluted with about 500 c.c. of distilled water. Two portions, each of 100 c.c., of this solution are then measured off (or more in special cases), to one of which 100 c.c. of distilled water are added and to the other 100 c.c. of the water under examination; after mixing each portion the liquids are allowed to stand for two to three minutes, a small crystal of potassium iodide added to each, and the liberated iodine titrated with the  $N/100$  thiosulphate solution. The difference in the amounts of thiosulphate solution used in the two cases gives the value of the correction for 100 c.c. of water, which is calculated to the volume of water used for the estimation of the dissolved oxygen. The correction may be omitted if only an approximate determination of the oxygen is required.

Rideal and Stewart,<sup>1</sup> in using Winkler's iodometric method for the

<sup>1</sup> *Analyst*, 1901, 26, 141.

estimation of dissolved oxygen in water, recommend first oxidising the organic matter and nitrites present by means of an  $N/10$  potassium permanganate solution and concentrated sulphuric acid. The quantity of permanganate solution required is first determined by a preliminary test, and any slight excess used in the actual determination destroyed by the addition of a solution of neutral potassium oxalate.

Experiments by Fowler have shown that in presence of much oxidisable matter it is preferable to destroy the nitrites by the addition of urea, in acid solution.

By means of oxygen determinations the "rate of decay" of the water may also be investigated. For this purpose, air, filtered through cotton-wool, is passed for fifteen minutes through 1 to 2 litres of the water to be examined, in order to saturate it with air; it is then divided into calibrated bottles, which are closed with stoppers and inverted beakers filled with water, as described above. If the water originally contains much oxygen, it is unnecessary to pass air through. In one of the bottles the dissolved oxygen is at once determined; the others are kept in a dark place at the ordinary temperature, and the dissolved oxygen determined after standing for successive intervals of time, such as after one day, a few days, a week, etc. In an impure water a diminution of the oxygen occurs as part of it is used up, with the help of micro-organisms, in oxidising the organic matter in the water. The greater this diminution, the greater the rate of decay of the water. In the case of pure, natural waters the diminution is so small that it can scarcely be measured; in the case of waters containing much organic impurity and rich in bacteria it is distinctly appreciable, and in the case of sewage water it is considerable.

It is an interesting fact that in some waters, after exposure to sunlight, an increase in the oxygen may be observed; this is due to the presence of microscopic aquatic plants containing chlorophyll, which by their metabolism liberate oxygen from carbon dioxide.

The results by Adeney<sup>1</sup> illustrate the value of the determination of the dissolved gases in water (see Tables I. and II., p. 786).

The rate of decay of a water can be expressed in degrees, as the number of c.c. of dissolved oxygen per 100 c.c. of dissolved oxygen originally present, which disappear during the first twenty-four hours.

For purposes of comparison, the solubility of atmospheric air and of oxygen and nitrogen in water at various temperatures, is given in the table on page 787.

The data, which include recent determinations by L. W. Winkler,<sup>2</sup> give the volumes of the gases in air, free from carbon dioxide and ammonia, reduced to normal temperature and pressure, which saturate 1000 c.c. of water at 760 mm. pressure.

<sup>1</sup> *Loc. cit.*

<sup>2</sup> *Ber.*, 1901, 34, 1419.

Under the same conditions 1000 c.c. of water dissolve the following volumes of methane:—at 0°, 55.30; at 5°, 47.64; at 10°, 41.27; at 15° 36.28; at 20°, 32.33; at 25°, 29.13; and at 30°, 26.48 c.c.

### I.—Samples of Water from the River Liffey, just above the Weir at Island Bridge, Dublin.

The dissolved gases expressed as volumes at N.T.P. per 1000 volumes of water; the other constituents as parts per 100,000.

Description of Samples.	Dissolved Gases.			Nitrogen as :—		Cl <sub>2</sub> .
	CO <sub>2</sub> .	O <sub>2</sub> .	N <sub>2</sub> .	NH <sub>3</sub> .	N <sub>2</sub> O <sub>5</sub> .	
Sample slightly turbid, yellowish-green tint; traces of suspended matter .	58.78	5.25	14.84	.0040	.034	1.26
Do. after keeping in closed vessel for thirty-seven days . . . .	62.13	0.88	14.25	.0015	.0385	...
Slightly turbid, brown colour; traces of suspended matter . . . .	41.38	7.49	15.55	.004	.027	1.21
Do. after fifteen days . . . .	42.12	6.54	15.45	.004	.035	...
Distinctly turbid, olive green tint; small quantity of vegetable debris in suspension . . . .	43.47	5.98	15.52	.002	.026	1.26
Do. after fifteen days . . . .	48.61	1.06	15.38	.035	.011	...
Turbid, yellowish-green tint; traces of suspended matter; collected during heavy rain after dry weather . .	72.64	3.23	14.93	.0028	.051	1.4
Do. after eight days . . . .	75.62	0.44	14.99	.023	.035	...

### II.—Samples of Well-Waters.

The dissolved gases expressed as volumes at N.T.P. per 1000 volumes of water; the other constituents as parts per 100,000.

Description of Samples.	Dissolved Gases.			Nitrogen as :—		Cl <sub>2</sub> .
	CO <sub>2</sub> .	O <sub>2</sub> .	N <sub>2</sub> .	NH <sub>3</sub> .	N <sub>2</sub> O <sub>5</sub> .	
Sample clear and colourless, with minute traces of suspended matter	205.10	5.64	14.83	.002	.12	3.5
Do. after thirty-four days . . .	204.72	5.32	14.70	.000	...	...
Sample slightly turbid, colourless, and free from suspended matter . .	113.69	4.03	15.69	.016	.254	5.9
Do. after twenty-one days . . .	113.54	3.76	15.78	.000	...	...

### Hydrogen Sulphide.

Hydrogen sulphide occurs in some ground waters, but usually in such small amount that it is best determined colorimetrically, rather than by the iodometric method proposed by Dupasquier and Fresenius.<sup>1</sup>

<sup>1</sup> Cf. Fresenius, *Quantitative Analysis*, 7th ed., 1876, vol. i., p. 381; also, Tiemann-Gärtner, *loc. cit.*, p. 227.

If water containing hydrogen sulphide is treated with Rochelle salt solution (to prevent the precipitation of calcium and magnesium carbonate) and an alkaline solution of a lead salt, it is coloured more or less brownish, according to the amount of hydrogen sulphide present. By comparing the coloration with that given by a dilute sulphide solution of known strength, the quantity of hydrogen sulphide present in the water can be estimated. As a standard solution, L. W. Winkler<sup>1</sup>

Temperature.	Oxygen. c.c.	Nitrogen, Argon, etc. c.c.	Total. c.c.	Percentage of Oxygen in the Dis- solved Air.
0	10.19	18.99	29.18	34.91
1	9.91	18.51	28.42	34.87
2	9.64	18.05	27.69	34.82
3	9.39	17.60	26.99	34.78
4	9.14	17.18	26.32	34.74
5	8.91	16.77	25.68	34.69
6	8.68	16.38	25.06	34.65
7	8.47	16.00	24.47	34.60
8	8.26	15.64	23.90	34.56
9	8.06	15.30	23.36	34.52
10	7.87	14.97	22.84	34.47
11	7.69	14.65	22.34	34.43
12	7.52	14.35	21.87	34.38
13	7.35	14.06	21.41	34.34
14	7.19	13.78	20.97	34.30
15	7.04	13.51	20.55	34.25
16	6.89	13.25	20.14	34.21
17	6.75	13.00	19.75	34.17
18	6.61	12.77	19.38	34.12
19	6.48	12.54	19.02	34.08
20	6.36	12.32	18.68	34.03
21	6.23	12.11	18.34	33.99
22	6.11	11.90	18.01	33.95
23	6.00	11.69	17.69	33.90
24	5.89	11.49	17.38	33.86
25	5.78	11.30	17.08	33.82
26	5.67	11.12	16.79	33.77
27	5.56	10.94	16.50	33.73
28	5.46	10.75	16.21	33.68
29	5.36	10.56	15.92	33.64
30	5.26	10.38	15.64	33.60

recommends an ammoniacal solution of arsenic trisulphide of such concentration that 1 c.c. corresponds to 0.1 c.c. of hydrogen sulphide gas at 0° and 760 mm. pressure.

For the estimation of small amounts of hydrogen sulphide in natural waters the following solutions are needed:—

1. Twenty-five g. of crystalline Rochelle salt, 5 g. of sodium hydroxide, and 1 g. of lead acetate are dissolved in 100 c.c. of water.
2. 0.0367 g. of pure, dry arsenic trisulphide are dissolved in a few

<sup>1</sup> *Z. anal. Chem.*, 1901, 40, 772.

drops of ammonia and the liquid diluted to 100 c.c.; 1 c.c. of this solution corresponds to 0.1 c.c. of hydrogen sulphide gas at 0° and 760 mm. pressure. The arsenic trisulphide is prepared by adding a solution of 1 g. of arsenic trioxide in dilute hydrochloric acid to 100 c.c. of freshly prepared hydrogen sulphide water and drying at 100°, after washing. The ammoniacal solution does not keep, and is therefore prepared as required for use.

The estimation is carried out as follows:—One hundred c.c. of the water to be examined are poured into a colourless glass bottle of about 150 c.c. capacity in which 5 c.c. of reagent No. 1 have been previously placed. One hundred c.c. of distilled water and 5 c.c. of the reagent are treated in a similar bottle with the ammonium thioarsenite solution, which is added from a small, narrow burette, until the colorations in the two bottles are equal. The number of c.c. of ammonium thioarsenite solution used is equal to the number of c.c. of hydrogen sulphide contained in a litre of the water.

If a more exact determination is required, the water is passed through a stoppered bottle of rather more than 100 c.c. capacity, at the source of supply, until the initial contents of the collecting bottle have been thoroughly replaced, the bottle completely filled, 5 c.c. of reagent No. 1 run into the bottom of the liquid from a long, narrow pipette, the bottle closed, and the contents thoroughly mixed. The hydrogen sulphide is then estimated in 100 c.c. of the liquid, using 95 c.c. of distilled water and 5 c.c. of the reagent for comparison. The hydrogen sulphide content of the original water is then obtained by calculating the amount found in 100 c.c. of the sample.

This method has the advantage that the results are not affected by the presence of thiosulphates, which are usually contained in sulphuretted waters. If less than 0.2 c.c. of hydrogen sulphide per litre is present, from 500 to 1000 c.c. of the sample are taken for the estimation; if more than 1.5 c.c. per litre are present the coloration is too great, and it is then best to employ the iodometric method of Dupasquier and Fresenius.

If the water containing hydrogen sulphide is coloured, neither the colorimetric nor the iodometric method can be used. In this case the hydrogen sulphide must be expelled by means of carbon dioxide, generated in the liquid, and the gaseous mixture passed through bromine water, which oxidises the hydrogen sulphide to sulphuric acid. The estimation is carried out as in the determination of the total carbon dioxide (p. 763), 20 g. of coarsely granular calcite, which does not give off any hydrogen sulphide on treatment with acid, being used instead of metallic zinc; the volume of this weight of calcite is = 7.2 c.c. A collecting bottle of 500 c.c. capacity is used, in which it is best to place the calcite before collecting the water. For the estimation, the glass

vessel *b* (Fig. 185, p. 763) is placed in position, connected with a small wash-bottle containing dilute bromine water free from sulphuric acid, and 50 c.c. of concentrated hydrochloric acid then gradually added through the dropping-funnel. After the evolution of gas has ceased the bromine water is evaporated to a small bulk and the sulphuric acid formed determined gravimetrically.

#### MICROSCOPIC EXAMINATION

The object of the microscopic examination of water is to determine whether direct pollution has occurred either by means of polluted feeders, or of insufficient earth-filtration, or by the introduction of fæces, domestic refuse, or similar impurities. Such water, in addition to being offensive, often contains pathogenic germs, and must, of course, be rejected, both as a drinking water and as a supply water for domestic purposes.

The microscopic examination is carried out by observing the sediment with a magnification of from 50 to 500. If the water is perceptibly turbid it is allowed to settle in the collecting bottle for twenty-four hours. A little of the sediment is then removed by closing the upper end of a glass tube with the finger, immersing it quickly to the bottom of the bottle, and opening it so that a little of the sediment enters; the tube is then closed again with the finger, carefully removed from the bottle, and a small drop of the contents placed on the object glass and covered with a cover-glass. If the water is not noticeably turbid it is first allowed to settle in the collecting bottle, the larger part carefully decanted off, and the remainder poured into a conical test-glass; after standing overnight, a sample of the deposit is taken from the bottom of the glass as described.

The sediment from an unpolluted water consists mainly of mineral fragments. Green algæ and infusoria also often occur. The impurities for which the water must be more especially examined are meat-particles which have passed through the intestines and been coloured yellow by gall, the eggs of parasites of the human or animal intestine, domestic refuse such as starch grains, wool-, hemp-, or cotton-fibres bits of paper, etc.

Further details concerning the microscopic examinations of water will be found in the following more special works:—

Tiemann-Gärtner, *Untersuchung und Beurteilung der Wässer*; C. Mez, *Mikroskopische Wasser-Analyse*; J. C. Thresh, *The Examination of Water and Water Supplies*; and G. C. Whipple, *The Microscopy of Drinking Water*.

#### BACTERIOLOGICAL EXAMINATION

The purpose of the bacteriological examination is to determine the number of living bacteria and bacterial spores present in the water,

and also to test for the presence of pathogenic bacteria such as cholera, typhus, etc. The recognition of specific bacteria involves a full bacteriological examination, but the number of bacteria can be counted with comparative ease, and in a chemical laboratory.

The number of spores capable of development can be determined by inoculating lukewarm and therefore liquid gelatine solution, so-called "nutrient gelatine," with a measured sample of the water. The nutrient gelatine sets on cooling, and so fixes the bacteria; both the bacteria and their spores multiply quickly in the gelatine, and, as they cannot disseminate, they form colonies which become visible to the naked eye in the course of a few days. By counting the number of colonies, the number of germs in the sample, capable of development, is determined.

The sample for the bacteriological examination should be taken with special care and be collected in a small, glass-stoppered bottle. The bottle is first sterilised by prolonged heating in an air-bath at 150°, only opened just before collecting the sample, and closed immediately afterwards. If the sample is collected from the main the water must first be allowed to run for some time; similarly, in the case of a well provided with a pump, the water should be pumped through for about ten minutes. Samples of spring water or of surface water are taken with a bottle fastened to a wire, which is filled by simple immersion. It is most important to remember that the bacterial contents of a water may increase considerably on standing for even less than a day, and any delay should therefore be avoided in making the examination. The original bacterial contents of the water may be preserved for from one to two days by enclosing the bottle in a suitable tin and packing it in ice.

A single bacteriological examination is seldom sufficient for any definite view to be formed as to the character of a water supply; a series of tests are really necessary, which should be made at suitable intervals, such as in summer and winter, before and after a rainy period, at high and low water, etc.

The preparation of nutrient gelatine suitable for the culture of water-bacteria, and its sterilisation, and the method of counting bacteria, etc., are described below, as they are operations which can be carried out in any chemical laboratory, without any special bacteriological equipment.

**Preparation of Nutrient Gelatine.**—Twenty g. (22 g. in summer) of finest, dry gelatine, cut into small pieces, are placed in a flask, 200 c.c. of distilled water added, and the whole warmed on the water-bath, with thorough shaking, until complete solution takes place. This gelatine solution is then clarified by the addition of 10 c.c. of a solution of fresh white of egg mixed with an equal volume of distilled

water. • The liquid is then warmed on the water-bath until the albumin has coagulated in flakes, the solution poured through a large, pleated filter paper, and the filtrate, which is at first turbid, poured back on to the filter until it comes through clear; the whole is then placed in a drying-oven at about  $40^{\circ}$ . The filtration takes about two hours. The filtrate, which is somewhat acid, is treated with sodium hydroxide solution till sensitive blue litmus paper is just reddened; if too much alkali is added the solution becomes turbid after a short time.

Nutrient gelatine prepared in this way is quite suitable for the examination of water when it is only necessary to decide whether the sample is poor or rich in bacteria. It has been shown by parallel experiments that the addition of meat-extract, peptone, and salt, etc., for this purpose, is quite unnecessary.

When finished, about 10 c.c. of the nutrient gelatine is poured, whilst still warm, into each of a number of test-tubes, care being taken in introducing the nutrient gelatine that the upper part of the test-tube remains clean; the most convenient and cleanest method is to use a stopcock burette for this purpose. The test-tubes are then carefully closed with cotton-wool and placed in a suitable beaker, to which a wire handle is attached, for sterilisation; the beaker is lowered into a wider one, on the bottom of which a layer of straw and water, to a depth of a few inches, are placed. A dome-shaped cover is then placed over the larger beaker and the whole heated; the water is boiled vigorously for fifteen minutes from the time the steam begins to escape. The object of the sterilisation is to kill any bacteria, either contained in the gelatine or adhering to the cotton-wool or to the sides of the test-tubes. As, however, a single sterilisation at  $100^{\circ}$  does not infallibly destroy the spores of micro-organisms, the sterilisation is repeated on each of the two following days. The test-tubes containing the sterile gelatine are kept in a tin in a cool place; they will remain unchanged for months, as the cotton-wool plug prevents the entry of bacteria from the atmosphere. If the sterilisation has not been carried out with sufficient care colonies of bacteria may develop; such tubes must, of course, be discarded.

**Counting the Bacteria.**—The bacteria are grown in so-called "Petri-dishes," which are made of glass. The clean, covered dishes are first sterilised by heating to  $150^{\circ}$  to  $160^{\circ}$  for one hour in an air-bath, by which means adherent bacteria and spores are destroyed; after cooling they remain sterilised inside as long as they are kept covered. If special dishes are not available, ordinary crystallising dishes of about 10 cm. diameter, or conical Erlenmeyer flasks (Cramer) may be substituted, somewhat large crystallising dishes being used as a cover in the former case.

To take the sample of water to be examined, a glass tube, 15 to



20 cm. long and of about 5 mm. diameter, is drawn out at the end to a thin point so as to form a pipette; the thin end of the pipette is bent at an obtuse angle, the extreme end sealed in a flame before sterilising, and the wide end closed with a plug of cotton-wool. The pipette is then sterilised in the same way as the dishes.

The bacteriological examination should always be made either on the spot, or with the freshly collected sample. To take the sample, the point of the pipette is broken off, passed several times through a flame, to destroy any adhering bacteria, and then dipped into the sample; when 1 to 2 c.c. of the water have entered, the pipette is withdrawn and the water introduced into the sterilised culture-dishes; one drop is placed in the first dish, five in the second, and ten in the third, the dishes being half-opened for this purpose, and then closed again at once.

The water is then mixed with the sterilised gelatine. The gelatine is first liquefied by placing the test-tubes in water warmed to  $40^{\circ}$ , the melting point of the 10 per cent. nutrient gelatine being  $32^{\circ}$ ; after it is completely melted the cotton-wool plug is removed, the open end of the test-tube held for a moment in the flame to destroy any adhering bacteria, and the gelatine poured into the dish; care must, of course, be taken that the dishes are only opened for a very short time, to avoid the admission of bacteria from the air. The gelatine and water are then carefully mixed by moving the covered dish round in such a way that the liquid on the bottom acquires a circular motion. The number of drops of water added to each dish is noted on the lid and the dishes then placed on a horizontal plate, when the contents soon gelatinise. The volume of a drop delivered by the pipette is determined by counting the number of drops in 1 c.c.; if, for instance, there are forty drops per c.c., the volume of each drop is 0.025 c.c., and therefore the first dish contains 0.025 c.c., the second 0.125 c.c., and the third 0.250 c.c. of the water. After the contents of the dishes have set, they are kept at the ordinary temperature; they must not be exposed to direct sunlight.

After twenty-four to forty-eight hours little spots can usually be seen in the crystal-clear layer of gelatine; these are the bacteria colonies. If possible, one to two days are allowed to elapse so that the colonies may develop, before they are counted. If too long a time is allowed, the gelatine usually liquefies, or the colonies of mould fungi grow so rapidly that they cover the others. The dish, the contents of which appear the most suitable, is selected for counting the colonies. If the colonies are sparsely scattered in the dish they are all counted; for this purpose the dishes are inverted. In order to avoid error in counting, the positions of colonies already counted are marked in ink on the outside of the glass. If the colonies are closer together, the bottom of the dish is divided radially into fields with pen and ink or

with a glass-pencil, and the colonies counted separately in each field. If very many colonies have formed in the culture, they must not be allowed to grow large, but must be counted comparatively soon, with the help either of a simple lens or a so-called "thread-counter," which has an opening of 1 sq. cm. in the lower plate. The dish is inverted over a piece of black paper, and the number of colonies in 1 sq. cm. of several parts of the bottom of the dish counted; the total number of colonies is then computed from the mean of the number found in the sections examined. Thus, suppose that in the third dish, which contained ten drops = 0.25 c.c. of the water, sixteen colonies, on the average, had developed per sq. cm., and that the diameter of the dish was 10 cm., the area of the bottom,  $\pi r^2$ , = 78 sq. cm., and the total number of colonies =  $16 \times 78 = 1248$ ; therefore 1 c.c. of the water contains  $4 \times 1248$ , or approximately 5000 bacteria and spores.

As a check on the determination, it is advisable to conduct a parallel experiment with the nutrient gelatine by itself; if the examination has been properly carried out, either no colonies at all or only very few should develop in this dish; should any form, the number must of course be proportionately deducted from those formed from the water.

For further details on the bacteriological examination of water, the following works may be consulted:—Tiemann-Gärtner, *Untersuchung und Beurteilung der Wässer*; P. F. and G. C. Frankland, *Micro-Organisms in Water*; W. H. Horrocks' *Introduction to the Bacteriological Examination of Water*; J. C. Thresh, *The Examination of Waters and Water Supplies*.

#### INTERPRETATION OF RESULTS

Rain water is seldom used as a drinking water, both on account of its insipid taste and of its liability to contamination; when used, in default of a better source of supply, the surface from which it is collected and the store-tanks or cisterns should be kept as clean as possible.

Drinking water is usually ground water; spring water is the best drinking water, and a pure well supply is also good. Both spring water and well-water can be regarded as satisfactory from a hygienic standpoint, provided the spring is properly lined and covered, and the well is of the necessary depth, and further, provided that the adjoining soil is free from pollution, and that impurities cannot be extraneously introduced either by falling in or by flowing in, or contamination occur through inefficient earth-filtration from closets, cesspools, sewers, dung-heaps, stables, etc., in the vicinity. A well in a densely populated district will, however, seldom comply with these conditions. The water of artesian wells is very good drinking water if drawn from a sufficient depth and from a good substratum; it should then be clear, colourless

quantities of these substances (1 mg. or more per litre) indicate pollution with decaying nitrogenous matter, and therefore point to possible infection. The water of many artesian wells, however, may contain considerable quantities of ammonia and yet be quite admissible as drinking water or for domestic use, as in this case the presence of ammonia does not necessarily indicate pollution. From 1 to 5 mg. per litre of ammonia and traces of nitrous acid are normally present in rain water.

In judging a water in which traces of ammonia are found, every care must be taken to guard against contamination of the apparatus and of the liquids used in analysis, which may easily occur through the exceptional frequency of traces of this gas in the air of laboratories.

10. Pure spring and well-water contains extremely small quantities of organic matter. The oxygen-absorbing power (p. 742) of pure spring water usually amounts to scarcely 1 c.c. of  $N/100$  permanganate solution, and that of pure well-water to 1 to 2 c.c. per litre; the absorption of several c.c. of permanganate solution, and a considerable rate of decay (p. 785) are unfavourable indications. In the latter case, however, a water can only be rightly excluded for drinking or domestic use if nitrogenous organic matter is also present, as shown by the determination of the albuminoid or proteid ammonia.

11. The determinations of albuminoid and of proteid ammonia are to be regarded as the most important chemical methods of examination. Ammonia and nitrous acid are not only present in rain water, but may also be formed by the reducing action of micro-organisms on nitrates; if, however, more than traces of albuminoid or of proteid ammonia are found, decaying or unchanged, nitrogenous organic matter is certainly present, and is almost sure to be of animal origin. The determination of albuminoid ammonia is somewhat lengthy, and only gives reliable results if carried out with the most scrupulous care. The determination of proteid ammonia, on the other hand, is reliable and easy, and should therefore always be included in the analysis of drinking water. With regard to this newer method of investigation the following conclusions may be accepted provisionally:<sup>1</sup>—

- i. Pure natural water contains no proteid ammonia.
- ii. The amount of proteid ammonia may be considered as an index of the amount of nitrogenous organic matter present.
- iii. If the proteid ammonia present amounts to more than 0.1 mg. per litre the water is open to criticism from a hygienic standpoint; 0.2 mg. per litre may be considered as the maximum allowable quantity.

The same conclusions may be applied to the albuminoid ammonia.

If the reducing power is considerable, in absence of albuminoid or of proteid ammonia, this indicates that either organic matter of vegetable

<sup>1</sup> Cf. L. W. Winkler, *Z. anal. Chem.*, 1902, 41, 299.

origin only is present, or that the decay of organic matter of animal origin has reached its limit: that is to say, that the water has undergone a certain self-purification.

12. Phosphoric acid is only present in pure, natural waters, at most, in traces. The excrements of men and of animals being comparatively rich in phosphoric acid, the presence of more than traces indicates pollution by excreta.

13. Soft, natural waters, which at the same time contain free carbon dioxide and oxygen in solution, take up lead when passed through lead pipes. If lead, even in extremely minute traces, is introduced into the animal organism during a prolonged period, its action is highly injurious; waters containing lead are therefore to be considered directly injurious to health, and should not be allowed for purposes of consumption. As, however, hard water poor in carbon dioxide and oxygen may also dissolve traces of lead under certain circumstances, and as, on the other hand, lead pipes are still largely used for the narrower service pipes on account of their cheapness and convenience, it is often unavoidable to pass traces of lead. The presence of some tenths of an mg. of lead per litre is of serious importance, and water containing 1 mg. of lead or more per litre must be described as poisonous.<sup>1</sup>

14. If, in the bacteriological examination, not more than 100 colonies of bacteria develop per c.c. the water contains few bacteria; such water is, however, seldom supplied, except from well-lined springs and very good filter-beds. The bacterial content of well-waters varies extremely widely; the number of germs capable of development per c.c. may be less than 100, or many thousands; surface waters from inhabited districts are especially rich in bacteria.

For drinking and domestic purposes, waters comparatively rich in bacteria are to be avoided as far as possible, and those distinctly rich in bacteria must be excluded. If pathogenic bacteria are present, the water must always be condemned as extremely dangerous, both for drinking and domestic purposes.

Lunge has pointed out that the absolute number of bacteria in water varies so much that serious mistakes may be committed if the water is judged on this basis without taking all the other circumstances into consideration. The value of counting the bacteria is chiefly as a control of the efficiency of purifying plant, such as filter-beds, etc.

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## FEED WATER FOR BOILERS AND WATER FOR OTHER TECHNICAL PURPOSES

By Professor G. LUNGE.

THE examination of feed water for boilers and of water for other technical purposes is considerably simpler than that of drinking water. It is only in exceptional cases that a water supply for technical use contains such large quantities of chlorides, nitrates, and organic matter as to necessitate a quantitative estimation; should this be required, however, the methods described above (pp. 750 and 751) may be used.

In most cases the chief constituents of importance are the alkaline earths, and especially the bicarbonates and sulphates of calcium and magnesium. These compounds constitute the "hardness" of the water, which is expressed in units of  $\text{CaO}$  or  $\text{CaCO}_3$  per 100,000 parts of water, the magnesium salts being calculated into equivalents of  $\text{CaO}$ . An English degree of hardness is equivalent to 1 grain of calcium carbonate per imperial gallon of 70,000 grains, or 1.43 parts per 100,000. The value of French and German degrees of hardness is given on p. 739.

"Total hardness" denotes the total  $\text{CaO}$  and  $\text{MgO}$  calculated as  $\text{CaO}$ ; "permanent hardness," that which remains after boiling the water for some time, filtering, and diluting to the original volume with distilled water; the difference between total and permanent hardness is known as "temporary hardness." This latter, which coincides essentially with the amount of  $\text{CaCO}_3$  and  $\text{MgCO}_3$  deposited on boiling, and originally present as bicarbonates, which are determined by titration in a similar manner to alkalis, is therefore also known as the "alkalinity" (*cf.* p. 737). This term is justified, as the real alkalis do not occur in ordinary waters either as hydroxides or as carbonates, but only in mineral waters or in those to which alkali has been purposely added.

For the determination of the hardness, Clark's soap test (p. 740) was formerly generally employed. This test is empirical in character, and the results, which are only approximate, are not comparable under

varying conditions; it has accordingly been to a large extent replaced by more scientific methods (*cf.* p. 740), which are both more accurate and simpler.

For ordinary purposes the following determinations are sufficient:—

1. *Alkalinity.* Two hundred c.c. of the water are titrated in the cold with methyl orange and  $N/5$  or  $N/10$  hydrochloric acid, until the solution just shows a red tinge. It can be assumed, in the case of natural waters, that practically only calcium and magnesium bicarbonates have then been converted into the corresponding chlorides; the determination accordingly gives the temporary hardness of the water. The result is calculated into g. of  $\text{CaCO}_3$  per litre; if 200 c.c. of water are used, each c.c. of  $N/5$  hydrochloric acid required indicates 0.0500 g.  $\text{CaCO}_3$ , or 0.0280 g.  $\text{CaO}$  per litre. This method, which is generally known as *Hehner's method*, was described independently by Lunge in 1885.<sup>1</sup> The number of c.c. of  $N/5$  hydrochloric acid used in the titration, multiplied by 3.5, gives the hardness in English degrees; the value in French degrees is obtained by multiplying by 5, and that in German degrees by multiplying by 2.8.

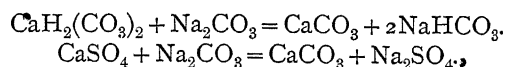
In the case of alkaline mineral waters, and also in that of a water supply purified by treatment with sodium carbonate, the "alkalinity" is not caused by the carbonates of the alkali earth metals, but mainly by sodium carbonate. In these cases the water is boiled in a porcelain dish for some time, in order to completely decompose the bicarbonates of the alkaline earths, the liquid then diluted to its original volume with distilled water, filtered, and the sodium carbonate determined as above in the filtrate.

Methyl orange is by far the best indicator in this case, and much to be preferred, especially to alizarin (p. 739), the use of which necessitates boiling, as with phenolphthalein, and is accordingly subject to the same disadvantages (*cf.* p. 71). Should there be any personal difficulty in following the colour changes, comparative solutions may be used with advantage.

2. *The Total Quantity of Alkaline Earths (Calcium and Magnesium)* is determined by precipitation with sodium carbonate solution whilst hot, whereby the calcium sulphate is also converted into the carbonate. An excess of sodium carbonate solution is used, and the liquid boiled in a porcelain dish, as glass might be slightly attacked. For very exact determinations, the liquid is evaporated to dryness, the residue heated to  $180^\circ$  and dissolved in hot water; the precipitate of alkaline earth carbonates is filtered off, washed with water as free as possible from carbon dioxide, dissolved in  $N/5$  hydrochloric acid, and the excess of acid titrated back with  $N/5$  sodium carbonate, with methyl orange as indicator. The quantity of hydrochloric acid used is equivalent

<sup>1</sup> *Die Wasserversorgung von Zürich*, 1885, p. 103.

to the quantity of alkaline earths, as above, and the decompositions are represented by the following equations:—



Each c.c. of  $N/5$  hydrochloric acid is equivalent to 0.0056 g. CaO, that is 0.028 g. per litre if 200 c.c. of the water are used.

An alternative method is to use a measured quantity of sodium carbonate solution and to determine the excess by titration. If, in the case of an ordinary water, free from sodium carbonate, the amount of alkalinity, determined according to 1 and expressed as CaO, is deducted from the total amount of alkaline earths, determined as above, also expressed as CaO, the amount of CaO which is present in the water as sulphate is obtained; every 28 parts of this CaO corresponds to 68 parts of  $\text{CaSO}_4$ .

The same procedure may be adopted in the presence of magnesium salts, but it is better in this case to use the mixture of equal parts of  $N/10$  sodium carbonate and  $N/10$  sodium hydroxide solutions recommended by Pfeifer and Wartha (p. 739). If sufficient excess of this reagent is used and the solution boiled for some time, the magnesium is precipitated as the hydroxide, which is much less soluble in water than the carbonate. Fifty c.c. of the mixed  $N/10$  solutions are usually sufficient for 200 c.c. of water. The boiling should be conducted in a porcelain dish or in a Jena-glass vessel; ordinary Bohemian glass should not be used.

3. *Sulphates.* For more exact analyses the sulphates, which may without error be calculated as calcium sulphate, are determined by precipitation with barium chloride from 200 c.c. of the water, either gravimetrically (p. 274) or volumetrically (p. 277). The gravimetric method is preferable, and is more exact than the volumetric estimation; also, as the quantity of precipitated barium sulphate is small, it is almost as quick as the latter.

4. *Magnesium* was formerly always determined gravimetrically, after previous precipitation of the calcium as oxalate, by precipitation as ammonium magnesium phosphate (p. 406). In the case of more exact analyses this method must be adopted; approximate determinations can be made by Pfeifer's volumetric method (p. 764).

5. *Iron* may occur in water in such quantity as to interfere with its use for bleach-works, dye-works, paper-mills, etc. On account of the small amounts usually present, colorimetric methods (p. 381) are the most suitable for its determination.

6. *Silica.* According to Reichardt,<sup>1</sup> silica may cause the formation of boiler-scale when present in very soft waters, but this is of



very exceptional. For exact analyses the silica should be determined; this is done gravimetrically according to the usual methods (p. 748).

7. *Chlorides* do not cause the formation of boiler-scale, but they may attack the iron of the boiler-plates; this applies especially to magnesium chloride. According to Ost,<sup>1</sup> the latter compound is the sole cause of this effect, but it can only occur in injurious amount in feed waters in extremely few cases. J. Pfeifer<sup>2</sup> is of opinion that the soluble magnesium salts react, at the pressure present in the boiler, with the calcium salts, forming readily soluble calcium salts and difficultly soluble magnesium compounds. Magnesium has an injurious effect because its carbonate becomes basic on boiling, and the carbon dioxide thus liberated assists the corrosion of the iron.

8. *Acid Waters* cannot of course be used for feeding boilers without previous treatment, preferably with lime. They occur only in mine waters (by weathering of sulphides) and in moorland waters.

*Special Tests to determine the amounts of Lime and of Sodium Carbonate necessary for the Treatment of Water:—*

1. Clear lime-water, previously titrated with  $N/5$  hydrochloric acid, using phenolphthalein as indicator, is added to 200 c.c. of the water under examination until the red coloration first appears and remains for a short time. Lime is not only used up, in this case, to convert calcium bicarbonate into the normal carbonate, but also to neutralise free carbon dioxide, and to precipitate organic matter, etc. As this is equally necessary on a large scale, this test indicates the amount of lime which must be added.

A more reliable plan is to add excess of lime-water, allow to stand for some time in absence of air, so as to exclude carbon dioxide, and then to titrate back the excess.

2. The turbid liquid obtained according to 1 is filtered, the filtrate treated with an excess of  $N/5$  sodium carbonate solution, again filtered, and the excess of alkali titrated back with  $N/5$  hydrochloric acid. In this way the quantity of sodium carbonate is found, which must be added to decompose the calcium sulphate present. Pfeiffer<sup>3</sup> prefers to evaporate the water to dryness with excess of titrated sodium carbonate solution, heat the residue to  $150^{\circ}$  to  $180^{\circ}$  to decompose the magnesium carbonate and thus render it insoluble, and to then extract it with water free from carbon dioxide, filter, and determine the excess of sodium carbonate in the filtrate.

Vignon and Meunier<sup>4</sup> first determine the amount of lime needed to fix the free and half-combined carbon dioxide as follows:—Fifty c.c. of the water are boiled with 50 c.c. of freshly distilled alcohol, which aids the precipitation of the calcium carbonate, and, after cooling, ten drops of

<sup>1</sup> *Chem. Zeit.*, 1902, 26, 819.

<sup>2</sup> *Z. angew. Chem.*, 1902, 15, 194.

<sup>3</sup> *Z. angew. Chem.*, 1902, 15, 193.

<sup>4</sup> *Comptes rend.*, 1899, 128, 683.

a 5 per cent. alcoholic phenolphthalein solution are added. The liquid is then titrated with a solution of lime-water containing 1.8 g.  $\text{Ca}(\text{OH})_2$  per litre at  $15^\circ$ , with shaking, until a permanent red coloration is obtained. A parallel, blank experiment is made for comparison with distilled water, with addition of 1 c.c. of lime-water.

If  $n$  c.c. of lime-water are used in the titration, the quantity of  $\text{CaO}$  required per litre of the water is:—

$$= \frac{n \times 1000}{50} \times \frac{1.8}{1000} \times \frac{56}{74} = n \times 0.027 \text{ g.}$$

The amount of sodium carbonate necessary to convert the chlorides and sulphates of calcium and magnesium into carbonates, is determined in a separate sample of the water by boiling 50 c.c. for five minutes in a nickel dish, making up to the original 50 c.c. with distilled water, adding 50 c.c. of alcohol, followed by phenolphthalein solution as above, and then titrating with a solution of sodium carbonate containing 1 g.  $\text{Na}_2\text{CO}_3$  per litre of water, until a red coloration is produced, equal to that of a blank prepared with distilled water and 3 c.c. of the sodium carbonate solution. If  $3+n$  c.c. of the sodium carbonate solution are used, then  $0.02 n$  g. of sodium carbonate are required per litre of water.

If it is desired to soften the water by treatment with sodium carbonate only, in the boiler, the amount necessary, as determined above for the decomposition of the contained chlorides and sulphates, must be added regularly; in addition, sodium carbonate, equivalent to the  $\text{CaO}$  determined as above, must be added at the start, once for all, as this part of the sodium carbonate is regenerated, the calcium and magnesium bicarbonates forming sodium bicarbonate, with precipitation of the carbonates of calcium and magnesium; the sodium bicarbonate is then further decomposed into sodium carbonate, water, and carbon dioxide; this relation does not hold strictly for magnesium compounds.

Pfeifer has drawn attention to the fact, which has been known for a long time but is often overlooked, that magnesium is precipitated from its compounds as magnesium hydroxide by excess of lime-water, and can therefore be determined by titrating back the excess of lime in the filtrate obtained in the estimation as above.

He represents the decompositions which occur in the softening of water by the following equations in which the behaviour of the magnesium compounds is taken into account:—

1.  $\text{CaH}_2(\text{CO}_3)_2 + \text{CaO} = 2\text{CaCO}_3 + \text{H}_2\text{O}.$
- 2a.  $\text{MgH}_2(\text{CO}_3)_2 + \text{CaO} = \text{MgCO}_3 + \text{CaCO}_3 + \text{H}_2\text{O}.$
- 2b.  $\text{MgCO}_3 + \text{CaO} = \text{MgO} + \text{CaCO}_3.$
3.  $\text{CaSO}_4 + \text{Na}_2\text{CO}_3 = \text{CaCO}_3 + \text{Na}_2\text{SO}_4.$
- 4a.  $\text{MgCl}_2 + \text{CaO} = \text{MgO} + \text{CaCl}_2.$
- 4b.  $\text{CaCl}_2 + \text{Na}_2\text{CO}_3 = \text{CaCO}_3 + 2\text{NaCl}.$

## 804 FEED WATER FOR BOILERS AND TECHNICAL PURPOSES

One molecular proportion of CaO must accordingly be allowed for each molecular proportion of either bicarbonate, and a second molecular proportion for each equivalent of MgO present in combination; an additional quantity is also required for the free carbon dioxide contained in the water. Further, one molecular proportion of  $\text{Na}_2\text{CO}_3$  is required for each molecular proportion of the compounds which cause permanent hardness. This corresponds to an addition of 8 mg. of CaO per litre of the water for each degree of temporary hardness, and of 56 mg. of CaO for every 40 mg. of combined MgO present, *i.e.* 1.4 mg. CaO per 1 mg. MgO; also  $\frac{106}{56} \times 8 = 15.1$  mg. of  $\text{Na}_2\text{CO}_3$  must be added, per litre, for every degree of permanent hardness.

The alkalinity or temporary hardness of a water and the total hardness can be determined by Wartha's form of Pfeifer's method (*cf.* p. 739). By subtracting the temporary hardness, the permanent hardness is obtained. If the total hardness is less than the alkalinity, the water contains sodium carbonate, and the addition of lime alone is necessary for purification.

Pfeifer regards the definition of permanent hardness, as the hardness of water after boiling for a long time, as altogether wrong; this should be called the "apparent" permanent hardness, as the solubility of magnesium carbonate varies with the temperature, and considerable differences are found according to whether the liquid is filtered hot or cold. The term permanent hardness should be restricted to that due to compounds other than the alkali earth carbonates.

To determine the magnesium, 100 c.c. of the water are titrated whilst boiling, with  $N/10$  acid, as in the determination of hardness, the carbon-dioxide-free liquid rinsed with boiled distilled water into a 200 c.c. flask, treated with a measured excess of lime-water (25 to 50 c.c., according to the total hardness), diluted to 5 c.c. above the mark, well shaken, cooled for a few minutes, poured through a large pleated filter paper, and the excess of lime-water titrated back in 100 c.c. of the filtrate. One c.c. of  $N/10$  lime-water corresponds to 2.0 mg. MgO. The strength of the lime-water used is determined by a blank experiment carried out in parallel with the estimation.

All the above determinations can be carried out in one experiment by using, for the estimation of the hardness, a mixed solution of sodium hydroxide and carbonate in which the relative amounts of the two substances have been determined by titration with successive additions of phenolphthalein and methyl orange (*cf.* p. 73). After the precipitation of the carbonates of calcium and magnesium, the proportions of sodium hydroxide and carbonate are again determined in the filtrate. To carry out this method, the water is titrated whilst boiling with  $N/10$  acid, rinsed into a measuring-flask, the sodium hydroxide-carbonate

solution added, and the whole diluted to 205 c.c.; the liquid is then allowed to cool, when the volume contracts to 200 c.c., filtered, and 100 c.c. of the filtrate titrated back as above, first with phenolphthalein and then with methyl orange. The first titration gives the temporary hardness; the total alkali used up, the total hardness; the sodium hydroxide used up, the magnesium; and the sodium carbonate used up, the calcium. This process, however, only gives approximate results, as the change of colour of the phenolphthalein is too gradual; the end-point of the reaction is in fact only accurate at a temperature approaching  $0^{\circ}$  and in presence of a large excess of sodium chloride (*cf.* p. 73).

Grittner<sup>1</sup> and Procter<sup>2</sup> have obtained good results by the Pfeifer-Wartha method. Blacher<sup>3</sup> has criticised it in various respects, especially in connection with the precipitation of the calcium and magnesium, which he regards as incomplete owing to the dilution to double the volume of the previously dilute solution. Also, he gives preference to the method for the determination of alkalinity described above (p. 800), and to the barium chloride method for the simultaneous estimation of sodium hydroxide and carbonate (p. 72). He accordingly adopts the following method of procedure:—One hundred c.c. of the water are titrated in a conical flask with  $N/10$  hydrochloric acid in the cold, using methyl orange as indicator; each c.c. of the acid is equivalent to 3.5 degrees of temporary hardness. Two hundred c.c. of the water are then similarly treated with the acid, a few drops in excess being added to avoid action on the glass. The liquid is then boiled down on a hot plate to 40 to 50 c.c., cooled, rinsed into a 100 c.c. flask which has a special mark indicating the volume of 100 c.c. of cold water at  $100^{\circ}$ , neutralised exactly, again heated to boiling, and 40 c.c. of a mixture of equal parts of  $N/10$  sodium hydroxide solution and  $N/10$  sodium carbonate solution added. The liquid is then boiled, diluted with boiling distilled water up to the mark, shaken up, poured through a pleated filter paper, the first 10 to 20 c.c. of the filtrate being rejected, into a stoppered flask, and cooled in running water. Meanwhile a neutral barium chloride solution is prepared by diluting 10 c.c. of a 10 per cent. barium chloride solution with 40 c.c. of water, neutralising whilst cold with  $N/10$  hydrochloric acid in presence of methyl orange, and heating to the boil. To this liquid, 50 c.c. of the above filtrate are added, followed by phenolphthalein solution, and the mixture titrated with  $N/10$  hydrochloric acid, whilst still warm, till colourless ( $=\text{NaOH}$ ), and then with methyl orange and phenolphthalein till red ( $=\text{Na}_2\text{CO}_3$ ). By this means any contact of the liquid with the gases from the burner, etc., is avoided. The proportions of sodium hydroxide and carbonate in the original mixture are similarly determined by a parallel experi-

<sup>1</sup> *Z. angew. Chem.*, 1902, 15, 847.

<sup>2</sup> *J. Soc. Chem. Ind.*, 1904, 23, 8.

<sup>3</sup> *Rigaer Industrie-Zeitung*, 1902, Nos. 23 and 24.

## 806 FEED WATER FOR BOILERS AND TECHNICAL PURPOSES

ment, and thus the quantity of  $\text{MgO}$  precipitated by the sodium hydroxide and that of the  $\text{CaO}$  precipitated by the sodium carbonate arrived at by difference.

The following combination of the methods of Pfeifer and of Blacher is recommended by Lunge as convenient and simple for the determination of the total hardness. A slight excess of hydrochloric acid is added to 200 c.c. of the water, the liquid boiled down to 40 to 50 c.c., rinsed into a 100 c.c. measuring-flask, exactly neutralised, after addition of methyl orange, with sodium hydroxide solution, 40 c.c. of a mixture of equal volumes of  $N/10$  sodium hydroxide and  $N/10$  sodium carbonate solutions added, heated to boiling, allowed to cool, diluted with distilled water up to the mark, poured through a dry, pleated filter paper, and the unused alkali titrated back with  $N/10$  hydrochloric acid and methyl orange in 50 c.c. of the filtrate. The number of c.c. of  $N/10$  hydrochloric acid used, multiplied by 2 and deducted from 40, gives the number of c.c. of  $N/10$  alkali used for the precipitation of the alkaline earths in 200 c.c. of the water. If required, the magnesium salts can be determined separately in the filtrate by Pfeifer's method (p. 804).

### LITERATURE

BOOTH, W. H.—*Water Softening and Treatment*, 1906.

CHRISTIE, W. W.—*Boiler Waters*, 1907.

Also the Literature given under the preceding section, "Drinking Water and Water Supplies," pp. 797-8.

## SEWAGE AND EFFLUENTS

By E. HASELHOFF, Ph.D., Director of the Agricultural Experiment Station, and Lecturer at the University, Marburg. English translation revised by GILBERT J. FOWLER, D.Sc., Lecturer in Bacteriological Chemistry in the Public Health Department of the University of Manchester, Consulting Chemist to the Manchester Corporation Rivers Committee.

OWING to the very varied character of effluents, and especially of those from the heavy and fine chemical industries, it is almost impossible to present a concise summary of the methods required for their analytical examination.

Effluents may be divided into those containing mainly mineral constituents and those consisting chiefly of nitrogenous organic substances. The examination of the former is essentially the same as that of drinking water, with a special regard to such abnormal constituents as are due to the particular industry concerned. Effluents containing mainly nitrogenous organic matter necessitate quite different methods of examination, which will be more specifically described in this section.

The constituents that may occur in the different kinds of effluents are summarised in the following list; owing to the great variations that may, however, exist in the character of effluents, the list is in no way to be regarded as complete.<sup>1</sup>

### I. Effluents containing mainly Mineral constituents from :—

1. *Coal mines* : Sodium, barium, calcium, strontium, and magnesium chlorides, ferrous and ferric sulphates, and free sulphuric acid.
2. *Strontianite mines* : Strontium, calcium, and magnesium carbonates or sulphates.
3. *Salt works and brine springs* : Sodium, calcium, strontium, and magnesium chlorides.
4. *Potassium chloride works, salt refineries, and bleach-works* : Calcium and magnesium chlorides and, from bleach-works, also manganous chloride.
5. *Pyrites mines, pyrites dressing works, and waste-heaps at coal mines* : Free sulphuric acid, ferrous sulphate, and sometimes zinc sulphate.

<sup>1</sup> Cf. J. König, *Die Verunreinigung der Gewässer, deren schädliche Folgen nebst Mitteln zur Reinigung der Schmutzwässer*, 2nd edition, 1899.

6. *Zinc blende mines, galena mines, and zinc blende stamping mills* : Zinc sulphate and bicarbonate.

7. *Wire works* : Free sulphuric acid and ferrous and ferric sulphates, or free hydrochloric acid and the corresponding chlorides, according to the cleaning liquor used.

8. *Galvanising works* : Free hydrochloric acid and ferrous chloride.

9. *Brass foundries and silver etching works* : Free sulphuric acid and copper sulphate.

10. *Pyrites residues* : Iron, zinc, or copper sulphates, and free sulphuric acid, according to the material used.

11. *Alkali works* : Calcium and sodium sulphides and polysulphides, calcium chloride, and calcium hydroxide.

12. *Slag waste-heaps* : Calcium and sodium sulphides.

13. *Bleaching works* : Calcium chloride and hypochlorite.

14. *Gas works and coke ovens* : Calcium and ammonium sulphides and thiocyanates, phenols, and tarry products.

15. *Potassium ferrocyanide works* : Sulphur and cyanogen compounds.

16. *Colour works and dye works* : Oxides of zinc, tin, lead, copper, and chromium, antimony, arsenic, dyes, and mordants.

17. *Electroplating works* : Potassium cyanide and free acids.

## II. Effluents containing mainly Nitrogenous Organic Matter.

These include the sewage of towns, and the effluents from slaughter-houses, sugar and starch factories, breweries, distilleries, dairies, paper mills, wool-combing works, cloth factories, glue factories, tanneries, etc.

In the majority of cases, in England, sewage and manufacturing effluents are treated together at the sewage purification works, and many of the analytical methods to be described are applied to the control of the method of purification adopted, more especially when the so-called "biological" or bacterial treatment of sewage is employed.

In the examination of all these effluents special attention must be directed to the amounts of suspended and dissolved organic matter, the amount of oxygen needed for their oxidation, and the amount of nitrogen in its various forms. In the case of effluents from breweries and distilleries attention must also be paid to the presence of yeast cells, dextrin, starch and sugars; the two latter constituents must also be considered in effluents from starch factories. The effluents from wool-combing works and from cloth factories must be tested for fats, soaps, and arsenic; effluents from tanneries for arsenic, and for sodium and calcium sulphides.

The variety in the composition of effluents is evident from this summary. It is to be borne in mind that the composition of the effluents from any one works is not always the same, but may vary

frequently even during a short period of time. It is therefore of the very greatest importance, for a correct examination of an effluent water, that the samples should be taken with care and judgment; incorrect sampling is more often the cause of an erroneous conclusion than the actual analytical examination.

### SAMPLING<sup>1</sup>

The vessels and corks used for taking the sample must of course be clean, and both should be thoroughly rinsed with the sample before filling. The sampling apparatus devised by F. C. G. Müller<sup>2</sup> is simple, convenient, and reliable, and permits of the sample being collected from any depth. It consists of a stirrup B (Fig. 192) soldered to a lead plate A, weighing 2 kilos, and suspended by means of the spiral spring E and the hook F, to a sounding-line. A bottle, D, of about 400 c.c. capacity, is fastened to the stirrup by means of the clamp C, and is fitted with a double-bored rubber stopper, both holes of which are closed by the U-shaped stopper H; the latter is attached to the chain J, which passes through the spiral to F, and is not quite taut.

To take a sample, the apparatus is lowered into the water and the line smartly jerked, when the stopper H will be removed, as the spiral spring elongates more quickly than the heavy mass below can follow; the water then enters through the small tube G placed in the one opening, whilst the air escapes through the other. After eighty seconds, at most, the bottle is filled and can be taken up.<sup>3</sup>

Müller has also constructed a special sampling arrangement for use with the "Tenax" apparatus, Fig. 194, p. 827.

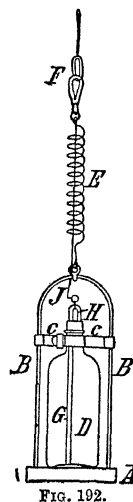


FIG. 192.

From 2 to 4 litres of the water must always be collected for examination.

• If a report on the water is to be made for a court of law or for an administrative authority, it is imperative that the samples should be collected by the responsible expert.

The most essential point in sampling an effluent water is that the sample should really represent a good average of the effluent. It is therefore necessary to determine whether the effluent flows continuously, and is of constant composition, or whether the composition alters during the course of a day, or whether the effluent only flows periodically

<sup>1</sup> A full account of the various forms of sampling apparatus is given by Schumacher, *Gesundheits-Ingenieur*, 1904, pp. 418, 434, and 454.

<sup>2</sup> *Forschungsber. a. d. biolog. Station zu Plön*, 1903, 10, 189.

<sup>3</sup> This apparatus is supplied by the Vereinigte Fabriken für Laboratoriumsbedarf, Berlin.



and not continuously during the whole day. In the first case, when the effluent flows continuously and is of uniform composition, it is unimportant at what hour the sample is taken. If the composition alters during the day, it is advisable to take samples at short intervals, of about ten to fifteen minutes, and to collect these together in a clean tub which has been previously well rinsed out with the effluent. The contents of the tub are then thoroughly mixed and a sample of the whole taken for analysis; or samples may be taken every ten to fifteen minutes, over periods of about two hours, at intervals during the day, and the whole mixed to obtain a final sample. For exact work, these samples should be mixed in proportion to the rate of flow at the time each was taken. This must be ascertained by a continuous gauging during the period of sampling.

If the effluent is discharged intermittently, the sample must be taken during the time that it is being run off; if the composition varies, a sample is taken each time the water is run off, and a mixture made of the samples thus obtained in the proportion of the actual quantities of water which they represent.

If the object of the examination is to test the efficiency of a method of purification, care must be taken that the purified water corresponds to the unpurified effluent. To satisfy this condition it is necessary to find out how long the effluent takes to flow through the purifying plant, and this time must be allowed to elapse between the collection of the samples of unpurified and purified water; the two samples must, of course, be collected in exactly the same manner.

When an effluent flows into a river, the question that has usually to be considered is whether the effluent has imparted such properties to the river water as are likely to be injurious to any of its specific uses. The mere detection of harmful constituents in the water is insufficient. Samples must be collected both above and below the point of entry of the effluent, and care taken that the sample collected above the point of entry has not mixed with the effluent through back-wash; it is also important to consider whether the water above the inflow of the effluent may have been previously contaminated by other effluents. The sample taken below the entry of the effluent must be collected at a point where the effluent has had time to thoroughly mix with the river water. This mixing is promoted by curves in the river, dams, bushes, etc. In the case of an even river with a slow current, effective mixing may only have been attained some miles below the point of entry of the effluent. In collecting the sample below the point of entry, it is also necessary to observe whether other feeders have supplied the river between the entry of the effluent and the place selected for taking the sample; should this be the case, a sample of each feeder must be collected and examined.

Samples should be taken from each bank and from the middle of the stream, also from the surface and from various depths, and the examination of the water made on a mixture of the samples collected in this manner; this method of taking samples from various parts is especially necessary in examining the water of stagnant pools, ponds, and lakes.

In the case of tidal rivers, the state of the tide must be noted and samples taken accordingly; pollution may, of course, be carried up the river on a rising tide.

In some cases, especially where many rapidly varying effluents flow into a stream, the extent of the influence or pollution of each effluent can be found by examining the composition of the water and determining, in addition, the quantity of flow of the stream and of each effluent; the degree of pollution introduced at high-, low-, and mid-water can then be calculated. The determination of the quantities of water is best dealt with by a hydraulic engineer.

Light may in some instances be thrown on the cause of pollution by an examination of the mud, or of the deposits on stones and plants, or by the presence of damaged plants and trees, or of dead fish. The fauna and flora of the water should be noted when collecting the sample.

## CHEMICAL EXAMINATION

### A. PRELIMINARY EXAMINATION ON THE SPOT

In the preliminary examination the following points are dealt with:—

1. *Appearance of the water.* Whether clear, turbid, coloured, etc. The extent to which a turbid or coloured water is harmful can only be determined by the examination of the suspended matter causing the turbidity; the turbid appearance of a water is not in itself decisive as to whether it is harmful or not.

2. *Smell.* Whether due to hydrogen sulphide, sulphur dioxide, free chlorine, ammonia, turnips, beet, yeast-water, etc.

3. *Reaction.* This is determined by holding litmus paper in the running water.

4. *Temperature.* A sensitive thermometer is held in the flowing water until it indicates a constant temperature; readings must be taken in various positions and at various depths. In sampling from manholes or other places where the actual liquid is not readily accessible, it is convenient to attach the thermometer to a small receptacle which can be lowered, along with the thermometer, into the liquid; the temperature can then be read without appreciable error, on bringing the receptacle to the surface.

5. *Nitrous acid.* A qualitative test with potassium iodide, starch

solution and dilute acetic acid, or with meta-phenylenediamine, is sufficient.

6. *Free Gases and volatile Acids.* If oxygen, carbon dioxide, hydrogen sulphide, chlorine, hydrochloric acid, etc., are to be quantitatively determined, this must either be done on the spot, or they must be fixed in such a way that they do not alter during transit. Oxygen can be absorbed either by L. W. Winkler's method (p. 782), or by that of C. G. Müller (p. 827), carbon dioxide by addition of lime-water free from carbon dioxide, hydrogen sulphide by addition of cadmium chloride, or of sodium arsenite and alkali, hydrochloric acid by silver nitrate solution, etc., and the solutions obtained further examined in the laboratory as described below.

7. *The Bacteriological examination* must be started on the spot, preferably in Petri dishes, and continued in the laboratory (*cf.* p. 789).

## B. EXAMINATION IN THE LABORATORY

The examination in the laboratory must always be made as soon as possible after the collection of the sample, especially if the effluent contains much organic matter; the latter readily decomposes on keeping, being partially converted into gaseous products, and partly causing solution of suspended organic matter, or the precipitation of organic substances from solution. If it is impossible to examine the sample at once, this must be taken into account in interpreting the results, or a preserving agent such as dilute sulphuric acid or chloroform must be added when the sample is collected. The former is used as an addition to filtered effluent waters in which the oxidisability, the organic nitrogenous compounds, ammonia, and organic carbon, are to be determined, and the latter as an addition to unfiltered water in which the residue on evaporation, the suspended matter, loss on ignition, nitric and nitrous acids and chlorine are to be estimated. Whenever possible, however, it is preferable to pack the samples in an ice box till they can be examined.

The above preliminary tests must be, as far as possible, controlled and repeated in the laboratory. The smell is often only noticeable after warming to 40° to 50°, or on rinsing round a small sample in a beaker.

When, in disputed cases, the water is examined by several chemists, uniform methods of analysis should be employed. The methods given below have, so far, been found to be trustworthy.

### 1. Residue on Evaporation and Loss on Ignition.

Two hundred c.c. of the water are evaporated to dryness in a previously ignited and weighed platinum dish; the residue is dried in

an oven at  $105^{\circ}$  to  $110^{\circ}$  for one hour, weighed after allowing to cool in a desiccator, and the drying repeated until the weight is constant.

The residue is then heated to redness in the platinum dish, moistened with ammonium carbonate and again gently ignited. The difference between the weight of the residue on evaporation and that obtained on ignition gives, fairly accurately, after allowing for water of crystallisation, the amount of organic matter in the water; the residue on ignition represents the anhydrous mineral matter.

## 2. Suspended and Dissolved Organic and Inorganic Matter.

From 200 to 1000 c.c. of the water, according to the amount of suspended matter present, are filtered through a filter paper previously washed, dried at  $100^{\circ}$  to  $105^{\circ}$ , and weighed. The residue on the filter is washed twice with distilled water, dried at  $100^{\circ}$  to  $105^{\circ}$ , and weighed, then ignited, and again weighed. The total residue represents the amount of suspended organic and inorganic matter, the ash, after deduction of the filter ash, the amount of inorganic matter, and the difference, the amount of organic matter.

To identify the inorganic constituents the ash is dissolved in hydrochloric or nitric acid, and the solution examined in the usual manner.

The dissolved inorganic and organic matter is determined in the filtrate and washings, from the above residue, or in an aliquot part, as described under 1.

If the water does not filter well, so that a change might occur during filtration, it is advisable to filter a well-mixed portion of the sample through a dry, pleated filter paper, and to determine the residue on evaporation and on ignition in 200 c.c. of the filtrate, and also in 200 c.c. of the original unfiltered water. The difference between the losses on ignition from the unfiltered and filtered water gives the amount of suspended organic matter, the difference between the residues on ignition, the amount of suspended mineral matter. The dissolved organic and inorganic matter are found, from the loss on ignition and the weight of the residue, from the filtered water.

If the water contains free lime, carbon dioxide is first passed through in excess, and the determinations then made as above; the carbon dioxide corresponding to the free lime is deducted from the total residue.

When the sample contains a large amount of suspended matter, *e.g.* storm water, a sufficiently accurate determination may be made by allowing, say, 500 c.c. of the sample to stand, when the greater part of the suspended matter settles out.<sup>1</sup> The fairly clear liquid is then syphoned off, and the deposit washed on to a smooth, toughened filter paper (*e.g.* Schleicher and Schüll, No. 575), washed, and dried in

<sup>1</sup> Fowler, *Sewage Works Analyses*, p. 106.

the air-bath at 100° to 110°. After drying, the suspended matter can be scraped off the smooth paper into a weighed crucible and weighed. On igniting, moistening with ammonium carbonate, and re-heating, the proportion of mineral matter is obtained as before.

Where a large number of determinations have to be made, they may be much facilitated by the use of a centrifugal machine. There are many types of these, all depending on the fact that if a solution containing suspended particles is rapidly whirled round, the particles tend to collect at the bottom of the liquid if they are heavier than the latter, and at the top if they are lighter. The separated particles can readily be washed by decantation, transferred to a crucible, dried, and weighed.

### 3. The Determination of Colloidal Matter.<sup>1</sup>

The organic and other matter in sewage and effluents is partly present in the colloidal state. The better the effluent the greater is the proportion of the total matter present in true solution, and the less the difference in composition before and after passage through a parchment membrane.

The best method for dialysis is to employ "sausage skin" dialysers filled with water and immersed in the solution to be dialysed, contained in long glass cylinders. The solution is left to dialyse until the chlorine content of the solution is found to be the same on both sides of the dialyser. A determination of the "oxidisability" or of the albuminoid ammonia, within and without the dialysers, will then give a measure of the ratio between the colloids and crystalloids thus:—

If  $x$  = value obtained for the solution outside the dialyser,  
 $y$  = value obtained for the solution inside the dialyser.

$$\text{Ratio: } \frac{\text{colloids}}{\text{crystalloids}} = \frac{x-y}{2y}$$

Similar information is more rapidly obtained when the liquid is clarified by boiling with sodium acetate and ferric chloride, filtered through paper, and the original liquid and the filtrate analysed.

In this case, 200 c.c. of the sample are treated with 2 c.c. of a 5 per cent. solution of ferric chloride, and 2 c.c. of a 5 per cent. solution of sodium acetate, the mixture boiled for two minutes, filtered, cooled, and the oxidisability or the albuminoid ammonia determined in both the unclarified and the clarified sample.

Then if:— $x$  = value obtained for the unclarified sample,  
 $y$  = value obtained for the clarified sample.

$$\text{Ratio: } \frac{\text{colloids}}{\text{crystalloids}} = \frac{x-y}{y}$$

<sup>1</sup> Cf. Kröhne and Biltz, *Hygienische Rundschau*, May 1904; Fowler and Ardern, *J. Soc. Chem. Ind.*, 1905, 24, 483; Fowler, Evans, and Oddie, *ibid.*, 1908, 27, 205; J. H. Johnston, *J. Royal Sanitary Inst.*, 1906.

#### 4. Oxidisability or Oxygen-consuming Power.

The quantity of potassium permanganate used up by a sample of water does not give an absolute measure of the amount of organic matter in a water, as the oxidisability of the organic substances varies greatly and is seldom complete under the conditions prescribed for the determination. Comparable values may, however, be obtained in the case of liquids of the same or similar origin.

The most satisfactory results are obtained by making the determination on the filtered sample of the water. In the case of comparative tests on purified and unpurified liquids, it is advisable to choose such dilutions that approximately equal quantities of permanganate are used for equal volumes of the diluted waters. The dilution should be such that the liquid remains red on boiling with 20 c.c. of  $N/100$  permanganate solution. The determination is carried out either in acid solution (Kubel) or in alkaline solution (Schulze). The former process is simpler and gives somewhat more constant results, but the oxidation of the organic matter is more complete in alkaline solution.

The details for the estimation are given under "Drinking Water," p. 742. As it is often necessary, in determining the reducing power of effluents, to dilute the sample with distilled water, attention should be paid to the fact that distilled water is seldom free from organic matter. H. Noll<sup>1</sup> has accordingly proposed to titrate the distilled water used with the permanganate solution, and to then immediately run 15 c.c. of  $N/100$  oxalic acid solution into the titrated liquid, and determine how much permanganate solution this requires; the difference between the two results gives the oxidisability of the distilled water, which is used as a correction in the determination. Or, a drop or two of permanganate solution may first be added to the water used for dilution or for making up the standard permanganate solution, till a very faint, permanent, pink tinge is obtained.

From the quantity of potassium permanganate solution required to oxidise the organic matter, the amount of the latter in the water may be expressed in various ways. Supposing that 10 c.c. of permanganate solution correspond exactly to 10 c.c. of oxalic acid solution, and that 10 c.c. of the former are originally added and 5 c.c. titrated back, then the 100 c.c. of water examined contain organic matter which requires 5 c.c. of permanganate solution, per litre, for its oxidation, or:—

$$\left. \begin{array}{l} 0.316 \times 5 \times 10 = 15.8 \text{ mg. potassium permanganate,} \\ \text{or } 0.08 \times 5 \times 10 = 4.0 \text{ mg. oxygen.} \end{array} \right\} \text{ per litre.}$$

If, as Wood and Kubel assume, one part of potassium permanganate oxidises, on the average, five parts of organic matter, then 1 litre of the water contains:—

$$1.58 \times 5 \times 10 = 79.0 \text{ mg. of organic matter.}$$

<sup>1</sup> *Z. angew. Chem.*, 1903, 16, 748.

The following methods of determining the oxygen-consuming power or oxygen-absorption are also used.<sup>1</sup>

*Four Hours' Test.* Fifty c.c. of the liquid, or, other volume, according to the reducing power, are treated with 10 c.c. of sulphuric acid (1 : 3) and 50 c.c. of potassium permanganate solution (10 c.c. = 1 mg. oxygen); the mixture is allowed to stand in a closed bottle for four hours, and is shaken from time to time if suspended matter is present. If the colour is noticeably weaker before the end of the four hours, more acid and permanganate are added. After four hours a few drops of 10 per cent. potassium iodide solution are added and the amount of liberated iodine determined by titration with sodium thiosulphate solution (1 c.c. = 2 c.c. permanganate solution); from this the amount of unused permanganate, and hence of absorbed oxygen, is calculated.

In other cases the duration of the action of the permanganate is limited to three minutes; this is called the *Three Minutes' Test*.

*Incubator Test.* The amount of oxygen taken up from the permanganate in the three minutes' test is first determined. A bottle is then completely filled with the sample, and kept closed, in an incubator, for six or seven days at 27°. The amount of oxygen absorbed in three minutes is then again determined. If putrefaction has taken place, the amount of oxygen absorbed in three minutes will have increased, in consequence of the greater oxidisability of the products of decomposition; if, on the other hand, the sample has remained fresh, no increase but possibly a slight decrease, will have occurred, due, in the latter case, to slight oxidation of the impurities at the expense of nitrates or of air dissolved in the water.

*Tidy's Method*<sup>2</sup> is similar to the preceding. The permanganate solution is allowed to act for two or three hours on the acidified water, and the undecomposed permanganate determined according to the method given under the four hours' test.

### 5. Alkalinity.

The alkalinity of a water may be caused by free calcium hydroxide, ammonia, etc. It is determined by titration with  $N/10$  or  $N/5$  hydrochloric acid, using methyl orange as indicator, and is expressed in terms of mg. of CaO per litre, or in mg. per litre of the principal base present. (Cf. pp. 737 and 764.)

### 6. Free Acids.

If alkalis or alkali earths are the only bases present, the free acids may be determined by titration with  $N/10$  sodium hydroxide solution, using litmus as indicator. If other metals (iron, zinc, copper) are also

<sup>1</sup> Cf. Fowler, *Sewage Works Analyses*, pp. 21-37.

<sup>2</sup> *J. Chem. Soc.*, 1879, 35, 66.

present, the total amounts of acids and of bases must be determined and calculated to salts; if there is an excess of total acids, that acid which, according to the nature of the effluent, may be supposed to be present in excess, is assumed to be free.

### 7. Nitrogen.

The quantity of total nitrogen and that of the individual nitrogen compounds is of special importance in forming a judgment on the character of an effluent.

*A. Total Nitrogen. The Kjeldahl-Jodlbaur Method.* Two hundred and fifty to five hundred c.c. of water are boiled down with 25 c.c. of phenol-sulphuric acid (200 g. phosphoric anhydride and 40 g. phenol in 1 litre of concentrated sulphuric acid) in a round-bottomed Jena-glass flask of about 700 c.c. capacity, over a naked flame; after cooling, 2 to 3 g. of zinc dust free from nitrogen, and 1 g. of mercury are added, the whole allowed to stand for a short time and then heated until the liquid is colourless. The residue is then treated as usual and the liberated ammonia absorbed by sulphuric acid. Full details of the method are given in the section on "Manures," Vol. II.

The following process, based on the Ulsch modification of the Kjeldahl method, has been found satisfactory for determining the total nitrogen in sewage and effluents. (Fowler.)

Fifty c.c. or more of the sample is taken and the free ammonia distilled off with steam after the addition of a little sodium carbonate. The liquid is then transferred to a 300 c.c. round-bottomed Jena flask, 2.5 g. of zinc dust and 1 drop of platinic chloride solution added, the volume made up to 150 c.c. with ammonia-free distilled water (carefully washing any adherent particles in the neck into the flask) and 10 c.c. of a 20 per cent. sulphuric acid solution added to the mixture. Care must be taken on the addition of the acid to prevent frothing over, by gently swirling the flask round, or by tilting it into an almost horizontal position, until most of the effervescence has subsided. The flask is then placed on a sand-bath in an inclined position and gently heated until the bulk is reduced to about 50 c.c.; after cooling, 0.1 g. of pure copper oxide is added and well mixed with the residue, and then 20 c.c. of concentrated sulphuric acid drop by drop, the same means being adopted as before to prevent frothing over; when the greater part of the effervescence has subsided, four more drops of platinic chloride are added, care again being taken to obviate frothing. The contents of the flask are then heated carefully over a small, free flame about 1 inch high, so that the flame does not reach the edge of the surface of the liquid; the heating is continued until the liquid is completely charred and has a pale green or greenish-grey colour. The contents of the flask are cooled, diluted carefully with ammonia-free



distilled water, the crystalline residue dissolved, the solution again cooled, transferred to a 300 c.c. flask and made up to the mark with the ammonia-free distilled water.

One hundred and fifty c.c. of this solution are placed in a round-bottomed flask fitted with a tap-funnel and attached to a condenser, the receiver of which dips into an Erlenmeyer flask containing 20 c.c. of  $N/10$  sulphuric acid solution; 2 or 3 drops of phenolphthalein are added to the solution, strong potassium hydroxide solution run in till alkaline, and the mixture distilled with steam until 200 c.c. have passed over into the sulphuric acid. A further 50 c.c. may be distilled over and tested for ammonia by Nessler's reagent. The excess of acid is titrated back with  $N/20$  potassium hydroxide, using methyl orange as indicator, and the result calculated in terms of nitrogen. A blank experiment should always be made with the reagents used.

If nitrates are present, the ammonia produced by their reduction, as determined in a separate experiment, must be deducted from the total amount found. It is safer, in this case, to determine the "nitrate" ammonia by starting two determinations as described, and determining the ammonia produced in the first stage of the process by stopping it at the end of the boiling down with dilute sulphuric acid and zinc dust, making alkaline, distilling with steam, and titrating or Nesslerising the distillate.

By subtracting the "albuminoid" ammonia, as determined by distillation with alkaline permanganate, from the total "organic" nitrogen, the amount of what may be termed "residual" nitrogen is obtained.

In the case of dry, solid matters such as sludge, 0.5 g. is taken for analysis, and the preliminary distillation of the free ammonia omitted.

J. Campbell Brown<sup>1</sup> recommends evaporating and subsequently igniting the sample in a glass or copper retort with a mixture of potassium hydroxide and potassium permanganate, the liberated ammonia being estimated by Nessler's solution; he states that this method is as precise as the Kjeldahl process and less troublesome to carry out.

*B. Ammonia.* (Cf. p. 765.) Ammonia is tested for qualitatively by adding 0.5 c.c. of sodium hydroxide solution and 1 c.c. of sodium carbonate solution to about 100 c.c. of the water, allowing to settle, and testing the clear liquid with Nessler's reagent; a pale yellow to reddish brown coloration or precipitate is formed, according to the amount of ammonia present.

For the quantitative determination, a definite volume of the water is distilled with ignited sodium carbonate, and the liberated ammonia either absorbed in titrated sulphuric acid or estimated colorimetrically. Ignited magnesia is sometimes used, but it is regarded by some writers

<sup>1</sup> *J. Chem. Soc.*, 1905, 87, 1051.

as likely to cause a decomposition of nitrogenous organic substances, and thus lead to high results.

The colorimetric method is only suitable for waters which do not contain a large proportion of ammonia; otherwise the sample must be largely diluted and the experimental error is then correspondingly increased. The preparation of solutions containing known amounts of ammonia for the colorimetric comparison is troublesome, and can be avoided by using a colorimeter with a permanent colour scale such as that devised by J. König.<sup>1</sup>

The colorimeter consists of six graded slips, each of which corresponds to the coloration produced by a certain percentage of ammonia, and which are arranged as the faces of a hexagonal prism, on a stand, so that they can be rotated round its vertical axis and successively compared with a tube containing the sample to be tested, which is supported on an arm of the same stand. Hehner's cylinders, with graduations at 25, 50, 75, and 100 c.c. are used for the sample, and the length and breadth of the slips is equal to the height and diameter of the cylinders respectively.

To carry out the determination, 300 c.c. of the water are treated with 2 c.c. of sodium carbonate solution (2.7 parts pure, crystallised sodium carbonate in 5 parts of water) and 1 c.c. of sodium hydroxide solution (1 part sodium hydroxide in 2 parts of water), shaken up, allowed to settle, and 100 c.c. of the supernatant liquid decanted into a Hehner cylinder, and 1 c.c. of Nessler's reagent added; if not clear, the liquid must be filtered through a filter paper previously washed free from ammonia. If a strong coloration, tending to red, appears at once, a second c.c. of Nessler's reagent is added, the whole well mixed, and the cylinder placed in the colorimeter and compared with the standard slips. Should the coloration be more intense than the darkest of the standards, the liquid must be correspondingly diluted.

For rapidly carrying out a large number of comparative determinations the Stokes colorimeter is very useful. This instrument consists essentially of two glass cylinders, each of 100 c.c. capacity, joined at the base by a rubber tube. One of the cylinders is graduated into c.c., and can slide in a clamp which is attached to a vertical brass support; the second cylinder is plain and rests on a sloping glass plate, beneath which a piece of white opal glass is placed. One hundred c.c. of ammonia solution of known strength, together with 4 c.c. of Nessler's reagent, are placed in these cylinders as the standard for comparison.

The sample to be tested is similarly treated with Nessler's reagent and placed in a third cylinder of corresponding dimensions. The graduated cylinder of the instrument is then moved up and down until the tints in the plain cylinder and in the third cylinder, containing the

<sup>1</sup> *Chem. Zeit.*, 1897, 21, 599.

sample, correspond. This identity of tint is best judged by observing the cylinders through a card perforated with two holes about half an inch in diameter, coinciding with each cylinder. From the reading on the graduated cylinder the amount of ammonia can then be calculated.<sup>1</sup>

*C. Nitrous Acid.* (Cf. p. 759.) To test qualitatively for nitrous acid, either a clear sample is used, or one which has been clarified by adding 3 c.c. of sodium carbonate solution (1 : 3), 0.5 c.c. of sodium hydroxide solution (1 : 2), and a few drops of alum solution (1 : 10). About 50 c.c. of the water are well mixed with 0.5 c.c. of zinc iodide-starch solution and 5 to 6 drops of dilute sulphuric acid.

The starch solution is prepared by dissolving 20 g. of zinc chloride in 100 c.c. of water, filtering, and adding to the boiling filtrate 4 g. of starch mixed into a thin paste with a few c.c. of cold water, with constant stirring. The whole is diluted to 1 litre, the flocculent material allowed to settle, and the solution filtered through a small jelly-bag.<sup>2</sup> Equal volumes of this solution and of potassium iodide solution are mixed for use.

A blue coloration is formed, which appears either at once or only after some minutes, according to the quantity of nitrous acid present; if the coloration appears only after about five minutes, it may be due to organic matter or to ferric salts. The error caused by the presence of ferric salts may be avoided by the use of a sulphuric acid solution of meta-phenylenediamine instead of the zinc iodide-starch solution. The test is then made by adding 1 to 2 c.c. of dilute sulphuric acid and 1 c.c. of the diamine solution to 100 c.c. of the water, in a tall glass cylinder. According to the amount of nitrous acid present, a brown or yellowish-brown to reddish coloration, due to the formation of an azo-dyestuff, is obtained.

The quantitative determination of nitrous acid is best effected colorimetrically. An accurate colorimetric method is that of G. Lunge and Lwoff (cf. p. 377). König's colorimeter has also been adapted for this estimation, and is very serviceable for the purpose. To carry out the determination, 100 c.c. of the clear or clarified sample are placed in a Hehner cylinder, 3 c.c. of zinc iodide-starch solution and 1 c.c. of dilute sulphuric acid added, and the coloration compared with the standards. The intensity of the coloration is entirely dependent on the duration of the reaction, and it is therefore advisable for each observer to first ascertain the time necessary, in minutes, for the coloration produced by a normal nitrite solution to correspond with the shades of the colour scale; this time must then always be kept to in making the test. If a strong blue coloration is formed at once, the liquid must be correspondingly diluted; if the reaction does not occur

<sup>1</sup> Cf. Fowler, *Sewage Works Analyses*, pp. 50-52.

<sup>2</sup> J. Thresh, *The Examination of Water and Water Supplies*, pp. 196 and 430.

in from five to six minutes, the amount of sulphuric acid is increased by 2 c.c. and another observation made after a few minutes.

Nitrites can also be determined colorimetrically by the metapenylenediamine method (*cf.* p. 759), or by means of sulphanilic acid and  $\alpha$ -naphthylamine (*cf.* p. 760).

*D. Nitric Acid.* Little importance is attached to the qualitative detection of nitric acid, in judging the character of an effluent, as the quantitative estimation of the amount present is essential. The qualitative tests are described in the section on "Drinking Water and Water Supplies," p. 751.

It is, however, often of value to obtain quickly an approximate idea of the quantity of nitrate present, and this can be effected by a method first worked out by J. Horsley<sup>1</sup> and subsequently brought into practical use by F. W. Stoddart. The following description of the method is given by G. McGowan:<sup>2</sup>—

Ten c.c. of the sample, filtered from all suspended solids, are poured into a test-tube of rather thick glass (a bacteriological test-tube 15 cm. long by 1.25 cm. diameter), about 0.2 g. of pyrogallol added, and the solution shaken till uniform; after the first two or three trials it is unnecessary to weigh the pyrogallol, as it can then be measured out with sufficient accuracy. Two c.c. of concentrated, nitrate-free sulphuric acid are then allowed to flow slowly down on to the bottom of the tube from a small pipette, plugged at the upper end with a piece of cotton wool, so as to form a layer below the water. Before withdrawing the pipette, its upper end must be closed by the finger, in order to prevent the acid still remaining in it from mixing with the aqueous layer of liquid. About 0.1 g. of pure, dry, powdered sodium chloride (the weight of which can also be judged after one or two trials) is then dropped into the tube, and falling—as much of it does—on the junction of the sulphuric acid and the water, it gives rise to a brisk effervescence. Should nitrate be present, a purple band is formed at the junction of the two liquids, the intensity of which is proportional to the content of nitrate.

A preliminary trial gives a rough idea of this amount, after which a second estimation is made along with three other simultaneous determinations with similar volumes of standard potassium nitrate solution. Thus, if the preliminary trial shows that about 0.6 parts of nitric-nitrogen are present per 100,000 parts of liquid, the three standards are made to correspond to 0.4, 0.6, and 0.8 parts. In this way the nitric-nitrogen in the sample may be gauged to within about 0.25 parts per 100,000. It is essential that the determinations should be carried out at the same time in both sample and standards, as it is

<sup>1</sup> *Chem. News*, 1863, 7, 268.

<sup>2</sup> *Reports of the Royal Commission on Sewage Disposal*, 1904, Vol. IV., Part V., p. 23.

useless to compare two tubes unless they have been prepared within a few minutes of one another; further, the sodium chloride used must be dry and finely powdered. There is considerable saving of time, in carrying out this test, if a number of dilute standard solutions of nitrate are always kept ready in stoppered bottles.

For the accurate quantitative determination of nitric acid Ulsch's method (p. 311) and the zinc-copper couple method (p. 753) have proved of value. The so-called zinc-iron method and the Schulze-Tiemann modification of Schlösing's method (p. 317) are also employed.

For the estimation, 1 litre of the water is evaporated down to 50 c.c. with addition of potassium hydroxide, free from nitrate, and finally, of a little potassium permanganate; the nitrate is then determined in the residue.

In the *Zinc-Iron Method*, the nitrate nitrogen is reduced to ammonia in alkaline solution; it is therefore convenient for the alkaline liquid prepared as above. The concentrated residue of the sample is treated in a flask with a little more potassium hydroxide, free from nitrate, and 75 c.c. of alcohol and 4 g. of a mixture of zinc- and iron-dust added; a little purified animal charcoal is also added to avoid frothing. The flask is connected with a condenser leading to a receiver which contains 10 c.c. of *N*-sulphuric acid. The whole is allowed to stand for from three to four hours, so that the violent evolution of hydrogen may subside, and is then distilled with a small flame. When all the alcohol has distilled over and water vapour comes off, the distillation is stopped. The excess of sulphuric acid in the receiver is titrated back with sodium hydroxide and the amount of nitrate-nitrogen calculated from the number of c.c. of sulphuric acid used up.

O. Böttcher uses in this method, for every 0.5 g. of sodium nitrate, 80 c.c. of sodium hydroxide solution of sp. gr. 1.3, 5 g. of zinc-dust and 5 g. of iron-dust (*Ferrum limatum*).

The *Schulze-Tiemann Modification of the Schlösing Method*, in which the nitric oxide evolved by reduction of the nitrate with an acid solution of ferrous chloride is measured, is carried out in the apparatus shown in Fig 193.

The small flask A, in which the reaction is affected, has a capacity of about 150 c.c., and is closed with a doubly-bored rubber stopper. The tubes *bc* and *de*, which pass through the stopper are joined, at *b* and *e* to the tubes *a* and *f* by means of rubber tubing provided with pinch-cocks; *bc* is drawn out to a fine point at *c*, about 2 cm. below the stopper, whilst *de* terminates flush with the bottom of the stopper. B is a glass trough filled with boiled-out 10 per cent. sodium hydroxide solution, and C a measuring tube graduated in 10 c.c. and filled with the same liquid.

The estimation is conducted as follows:—The concentrated residue of

the sample is rinsed into the flask A and further boiled down to 15 to 20 c.c., the pinch-cocks *b* and *e* being open. The lower end of the tube *d e f* is then dipped into the sodium hydroxide solution in the trough B and steam allowed to pass through for some minutes. When the steam has expelled all the air from the apparatus, the sodium hydroxide solution runs back into *e f* on closing the connection at *e* with the fingers, and a slight impact is felt. The pinch-cock at *e* is then closed and the liquid further boiled down to about 10 c.c., *a b c* remaining open. The

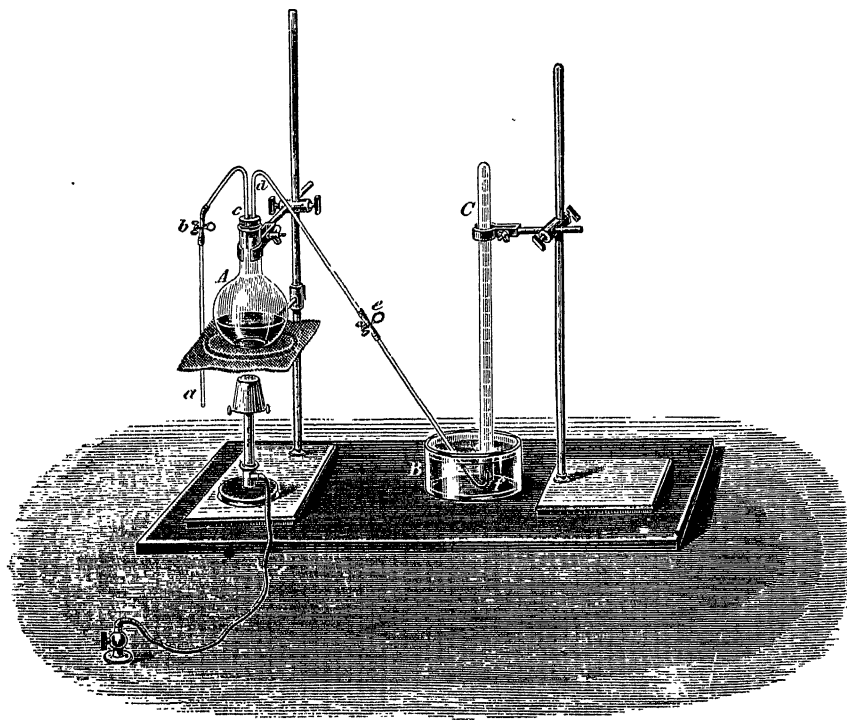


FIG. 193.

pinch-cock at *b* is then closed, the flame at once removed, and the tube *a* filled with water, taking care that no air remains at *b*. The measuring tube C is then placed in position so that the end of the delivery tube *d e f* projects for about 2 cm. into the former. When the rubber tubing at *b* and *e* has contracted, the tube *a* is dipped into a small beaker filled with 20 c.c. of boiled-out ferrous chloride solution. About 15 c.c. of this solution are then allowed to flow into A by carefully opening the pinch-cock at *b*. The tube *a* is then dipped into another beaker containing boiled-out hydrochloric acid, which is allowed to enter until all the ferrous chloride solution has been expelled from the tube *a b c*. The flask A is then gently warmed until the rubber

connections begin to distend somewhat and the evolution of gas checked by placing the fingers at *e*. When the pressure increases the evolved nitric oxide gas is allowed to pass slowly into the measuring tube C. Finally, the flask is heated more strongly until the volume of gas in C remains constant. The tube *ef* is then removed, and the measuring tube C transferred, by means of a small porcelain dish containing sodium hydroxide solution, to a large glass cylinder filled with water. After standing for half an hour, the temperature of the water, the barometric pressure, and the volume of the nitric oxide are read. Before measuring the volume of the gas the measuring tube is raised by means of a clamp until the liquid in the tube and in the cylinder is at the same level.

The volume found is reduced to 0° and 760 mm. pressure by means of the formula :—

$$v_1 = \frac{v(b-w)}{(1+0.00366t)} 760$$

where  $v_1$  is the volume at 0° and 760 mm. pressure,  $v$  the volume read,  $b$  the barometric pressure in mm.,  $w$  the tension of water-vapour, and  $t$  the temperature of the water; or the Tables VI.-VIII. (Appendix) may be employed for the correction. The weight of nitric anhydride in mg. is obtained by multiplying the number of c.c. of NO by 2.412.

As by this method any nitrous acid present in the water is also determined as nitric acid, 1.421 parts by weight of nitric anhydride must be deducted for every part of nitrous anhydride present.

When only small quantities of nitric acid are present the colorimetric brucine method of Lunge and Lwoff (pp. 379 and 751) is to be recommended.

*E. Suspended and Dissolved Organic Nitrogen and Ammonia.* Samples of 200 c.c. each, of the filtered and of the unfiltered water, or larger quantities if the water is poor in nitrogenous matter, are heated in hard glass Jena flasks of 500 to 600 c.c. capacity with acid sodium sulphite, ferrous chloride, and a few drops of sulphuric acid, and boiled down to 10 to 20 c.c.; this treatment destroys the nitric acid. The residue is then treated with 20 c.c. of concentrated sulphuric acid and the nitrogen determined by Kjeldahl's method. The difference between the nitrogen contents of the unfiltered and filtered water gives the amount of suspended nitrogen, and the nitrogen content of the filtered water, the amount of organic and ammoniacal nitrogen present in solution (cf. p. 813).

*F. Combined Organic Nitrogen. (Albuminoid Ammonia.)* The amount of so-called albuminoid ammonia is given by the difference between the organic and ammoniacal nitrogen found according to *E* and the ammoniacal nitrogen. For the direct determination the methods of Wanklyn, Chapman, and Smith (p. 769) are used.

### 8. Sulphuretted Hydrogen and Sulphides.

Small quantities of sulphuretted hydrogen are best determined colorimetrically. For this purpose 100 c.c. of the water are treated with 1 c.c. of sodium nitroprusside solution (2 g. per litre) and the violet coloration which is formed compared with a standard scale of colour, each shade of which represents a definite amount of hydrogen sulphide (*cf.* p. 786).

The titration of hydrogen sulphide with iodine solution is not reliable in the case of water containing much organic matter, but an approximate result may be obtained by this method by first determining approximately how much iodine solution is necessary to give a blue coloration with 200 c.c. of the sample. The volume of iodine solution required in this preliminary estimation is placed in a flask, 200 c.c. of the water introduced, the whole well shaken, starch solution added, and then more iodine solution, until the blue coloration is obtained.

Free hydrogen sulphide is best determined by passing air, freed from carbon dioxide by sodium hydroxide solution, through the water and absorbing the hydrogen sulphide carried off by the air, as lead sulphide, which is determined in the usual manner; or, the air containing hydrogen sulphide is passed into  $N/100$  iodine solution and the liberated iodine titrated. The soluble sulphides are determined in the residue by treating it with a solution of zinc acetate and acetic acid and weighing as zinc sulphide, or by oxidising to sulphuric acid and weighing as barium sulphate; in the latter case, any sulphuric acid originally present must, of course, be deducted.<sup>1</sup>

### 9. Chlorine.

*A. Combined Chlorine.* One hundred c.c. of the filtered water, or correspondingly less if the chlorine content is high, are heated to boiling, treated with a little potassium permanganate, and the boiling continued until the manganese oxides separate in a flocculent condition and the supernatant liquid remains clear. Any excess of permanganate used is decolorised by addition of a little absolute alcohol. The liquid is then filtered, the residue washed with hot water, and the filtrate and washings titrated with  $N/10$  silver nitrate solution (*cf.* pp. 123 and 750). One c.c.  $N/10$  silver nitrate solution = 0.003545 g. chlorine.

If much potassium permanganate has been used to oxidise the organic matter and the filtrate is alkaline, the chlorine may either be determined, as above, after neutralisation of the filtrate with nitric acid, or by preference gravimetrically, or by Volhard's volumetric method (p. 123).

*B. Chlorine in the Free State or as Hypochlorites.* From 100 to 500 c.c. of the sample are treated with 1 g. of potassium iodide and

<sup>1</sup> *Cf.* C. Weigelt, *Vorschriften für die Entnahme und Untersuchung von Abwässern und Fischwässern*, 1900, p. 20.



50 per cent acetic acid, and the liberated iodine titrated with  $N/10$  sodium thiosulphate solution; the titration is continued until a pale yellow coloration remains, freshly prepared starch solution then added, and the titration completed. One c.c.  $N/10$  sodium thiosulphate solution = 0.003545 g. Cl<sub>2</sub>.

The determination of chlorine or of hypochlorites in effluents has become of importance owing to the use of chloride of lime as a sterilising agent in certain cases. Acetic acid is used instead of hydrochloric in the titration, as the results are then unaffected by the presence of chlorates or of iron in the liquid.<sup>1</sup>

#### 10. Other Mineral Substances.

Lead, copper, iron, zinc, manganese, calcium, magnesium, potassium, sodium, and sulphuric acid are determined according to the usual methods. If these constituents are present only in very small amounts a correspondingly large quantity of the sample must be taken and previously concentrated with addition of a suitable acid.

Phosphoric acid is determined by evaporating from 500 to 2000 c.c. of the water, according to the quantity present, to dryness in a platinum dish, fusing the dry residue with sodium carbonate and potassium nitrate, dissolving the melt in nitric acid, and precipitating the phosphoric acid from its nitric acid solution with ammonium molybdate.

#### 11. Albuminoid Compounds, Sugar, Starch, and Yeast.

The biuret reaction is the most suitable for detecting the presence of albuminoid compounds in effluents. The water is treated with very concentrated sodium hydroxide solution and a few drops of a 1 per cent. solution of copper sulphate; in the presence of albuminoid compounds a reddish violet coloration is obtained.

Albuminoid substances can also be detected by means of Millon's reagent, which consists of a solution of one part of mercury in two parts of nitric acid of sp. gr. 1.42 diluted with twice its volume of water; it gives a rose-red coloration. In employing this test, the sample is concentrated, after first saturating with carbon dioxide if calcium is present, and precipitating any hydrogen sulphide with lead acetate, and then treated with the reagent at 60°. B. Proskauer<sup>2</sup> recommends the removal of hydrogen sulphide by shaking with litharge and then testing for albumin by the biuret reaction or with potassium ferrocyanide and acetic acid; the precipitate must also always be tested for undissolved albumin. In presence of albuminoid compounds which are precipitated by lead salts very little lead acetate is used, the whole warmed, the precipitate washed and digested with pepsin in a 0.5 per cent. solution of lactic acid; the liquid is then tested by the biuret reaction.

<sup>1</sup> Schultz, *Z. angew. Chem.*, 1903, 23, 833.

<sup>2</sup> Weigelt; *loc. cit.*

Effluents are tested for sugar, after concentration, either with Fehling's solution or by the ring test with  $\alpha$ -naphthol and concentrated sulphuric acid; the violet coloration obtained is a quick and delicate qualitative test. Starch and yeast are detected microscopically after centrifuging the sample.

## 12. Oxygen.

The method of L. W. Winkler is very suitable for the estimation of dissolved oxygen in water. It depends upon the fact that manganous hydroxide is converted by oxygen, in presence of alkali, into manganic hydroxide, which reacts with hydrochloric acid to form manganic chloride; this decomposes at once into manganous chloride and chlorine, which liberates iodine from a solution of potassium iodide; the liberated iodine is then titrated with sodium thio-sulphate solution. Details of this method are given in the section on "Drinking Water and Water Supplies," p. 782.

F. C. G. Müller<sup>1</sup> has constructed an apparatus, called the "Tenax" apparatus, for estimating the dissolved gases in water, which gives rapid and accurate results, and which can be used outside a laboratory.

The principal portion of the apparatus is the Tenax burette, shown in Fig. 194 in  $\frac{1}{10}$  of the natural size. It consists of a tube, A B C D, 10 mm. wide and with two U-bends, expanded at the top to form the funnel A, and drawn out to a width of 4 mm. below and expanded to a bulb at C. At the top of the bend, at B, a measuring tube E is attached of 4 c.c. capacity, graduated in  $\frac{1}{10}$  c.c. and fitted with a well-ground glass stopper F. This stopper also serves as a stopcock and allows communication to be made between the inside of the burette and the capillary tube P. The measuring tube is surrounded by the cooling vessel G. The lower part of the main tube is also surrounded by a cooling jacket H, which is fed from below, by means of the thistle funnel I, with water which escapes through the glass and rubber tubing shown in the figure. An outlet cock L is attached to the first bend of the main tube. The whole apparatus is clamped, in a vertical position, to a stand, for use.

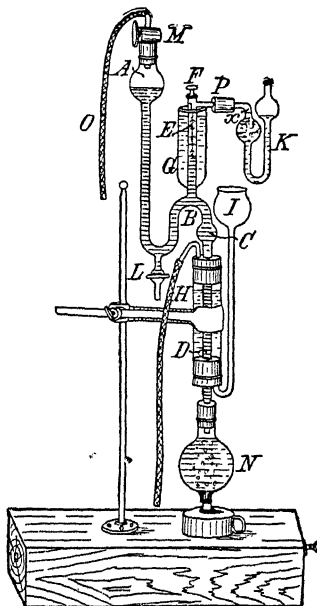


FIG. 194.

<sup>1</sup> *Forschungsber. a. d. biol. Station zu Plön*, 1903, 10, 177. The apparatus is supplied by the Vereinigte Fabriken für Laboratoriumsbedarf, Berlin.

To carry out a determination, the sample of water to be examined is placed in the flask N, of 100 c.c. capacity, and closed with a perforated rubber stopper plugged with a glass rod. The flask is attached to the narrow end of the main tube, as shown, after removing a glass rod used for keeping this end of the tube closed. Petroleum is then poured in at A, first filling the lower part of the main tube and then the measuring tube, E, the stopper F being open until the oil reaches a point close to the capillary of the side-tube P, when the stopper is closed, care being taken that no air-bubbles remain under the stopper. The cooling vessels H and G having been filled with cold water, the expulsion of the dissolved gases is commenced. For this purpose the water in the flask N is first heated to boiling with a large flame and then boiled for ten minutes with a small flame. The greater portion of the dissolved gases are expelled in the form of fairly large bubbles whilst the water is being heated up and when it starts boiling; this rises into the measuring tube, and thus drives some of the petroleum into the bulb A. During the boiling there should be a water-free space, filled with steam, in the upper part of the flask N and the lower part of the tube CD; care must be taken that the surface of separation of oil and water does not rise beyond the bulb C; should it do so, the flame is removed for a few seconds, thus causing the water to rush back. Cold water is passed through the cooler H, during the boiling, and also when the boiling is finished.

The whole of the gas in the sample is thus expelled and collected in the measuring cylinder. To read off its volume, oil is run off through the tap L until the levels in the open limb of the tube and in the measuring tube are the same. An interval of five minutes is allowed for the liquid on the sides of the measuring tube to run down; also, the meniscus must become sharp before taking the reading, as bubbles form in the viscous oil which only disappear slowly. If the time available for the estimation is limited, the process can be hastened as follows:—The opening A is closed, as shown in the figure, with a rubber stopper provided with a tap M and tubing O. By sucking sharply and intermittently through the tube the confining liquid in the measuring tube is made to fall and rise alternately, and by repeating this for five minutes the top of the meniscus can be distinguished. The volume is then read off, also the barometric pressure, and the temperature, as registered by a small thermometer placed in G. All the data for calculating the total volume are thus obtained.

The oxygen is then determined by absorption in the pipette K, which contains spirals of copper gauze, and which is filled to the bend with a solution made up of one volume of 10 per cent. ammonia solution, one volume of a saturated solution of ammonium sesquicarbonate, and two volumes of water. The pipette is connected by a

piece of thick-walled rubber tubing with the side-tube P of the measuring tube, and is kept attached during a number of analyses; after ten determinations the liquid must be renewed. The solution, which is itself colourless, becomes blue by absorption of oxygen.

The gas is driven into the pipette by opening the stopcock F, and blowing at O, and is similarly drawn back into the measuring tube after absorption, by suction. Care should be taken to avoid oil getting into the pipette, or the absorption liquid into the measuring tube. After the absorption of the oxygen is complete, the reading of the volume of residual nitrogen is taken as described above.

If several successive determinations are made over intervals up to several days, the oil is allowed to remain in the apparatus and the flask in position. After closing all the cocks, the flask can be removed without loss of oil, and replaced by a flask containing another sample; the work is then continued as described.

If after a determination the measuring tube is very greasy, it is cleaned with a small roll of blotting paper after lowering the oil by sucking at O and closing M. If the determinations follow one another immediately, the flask is immersed in cold water before removal, so that it is cooled down for the next determination. The water in G is also syphoned off and replaced, if it has become appreciably warm.

The readings of the measuring tube can be checked by calibrating it against an accurate tube of the same diameter, by running successive portions of the oil into the latter from L and noting the corresponding volumes in the measuring tube E, the apparatus having been first filled as described above.

It is to be noted that the gases are not absolutely insoluble in the oil used as the confining liquid. If ordinary burning-petroleum, saturated with air, is used, rather too little oxygen is found in the case of gases rich in the latter, and rather too much with gases poor in oxygen. This error is in most cases unimportant, but high-boiling petroleum oil of sp. gr. 0.87 is preferable, although considerable foam is caused by its use. This oil dissolves oxygen so slightly and so slowly that no perceptible error is caused under the conditions of the determination.

The Adeney apparatus described on p. 780 is very suitable for investigating the changes in composition of the dissolved gases, due to fermentation of the organic matter, in mixtures of sewage and water.

### 13. Organic Carbon.

The amount of potassium permanganate necessary for oxidation is no exact measure of the amount of organic matter present in water. Not only do the different organic compounds which may be present need varying amounts of oxygen for oxidation, but in addition inorganic

compounds, such as ferrous salts, nitrites, and sulphur compounds, which occur fairly often in effluents, absorb part of the oxygen of the permanganate. In order to establish a trustworthy method for the estimation of organic carbon, J. König<sup>1</sup> has worked out the following method devised by P. Degener,<sup>2</sup> which is based on the conversion of all the carbon of the organic compounds, after removal of pre-formed carbon dioxide, into carbon dioxide, by oxidising agents; the carbon dioxide thus formed is absorbed by alkali and weighed.

*A. Organic Carbon in the Filtered Water.*—Five hundred c.c. of the water are quickly filtered, if turbid, through a large Gooch porcelain or metallic crucible of about 100 c.c. capacity, fitted with asbestos, and the

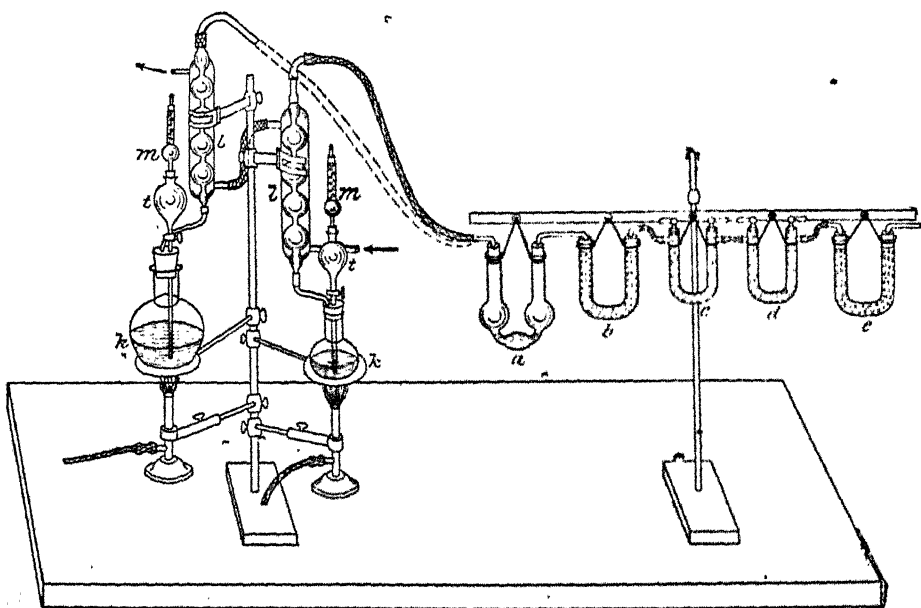


FIG. 195.

drained residue washed with distilled water. In the case of waters which do not filter well, the filtration may be assisted by precipitation with a solution of iron- or aluminium-alum and disodium phosphate without affecting the results. The filtrate is placed in the round-bottomed flask *k*, Fig. 195, together with 10 c.c. of dilute sulphuric acid, and the flask connected with the condenser, but not with the other parts of the apparatus. The water is then boiled for half an hour, with open condenser and continuous condensation, until all pre-formed carbon dioxide has been expelled. It is then allowed to cool and 3 g. of potassium permanganate, 10 c.c. of a 20 per cent. mercuric sulphate solution, and a further 40 c.c. of dilute sulphuric acid added; the flask is

<sup>1</sup> *Z. Unters. Nahr. u. Genussm.*, 1901, 4, 193.

<sup>2</sup> *Z. Ver. deut. Zuckerind.*, 1882, 32, 59.

then again attached to the condenser, and the latter connected up with the absorption tubes as shown in the figure. The Peligot tube *a* is filled up to the bottom of the bulbs with about 20 c.c. of concentrated sulphuric acid; tube *b* contains calcium chloride, *c* and *d* soda-lime, and *e* half soda-lime and half calcium chloride. The flask *k* is closed with a double-bored rubber stopper, which carries a glass tube leading to the condenser, and a dropping-funnel *z*, provided, with a soda-lime tube *m*. The condenser retains the bulk of the water-vapour which is formed, and the tubes *a* and *b* absorb the last traces; the tube *e* prevents access of water-vapour and of carbon dioxide from the air. The tubes *c* and *d* serve to absorb the carbon dioxide formed by the oxidation, and are weighed before and after the experiment. Strong potassium hydroxide solution may also be used to absorb the carbon dioxide, but it has the disadvantage that loss by spirting may occur should the liquid in the flask bump, which is often the case during the oxidation of suspended matter. After connecting up the apparatus, the flask *k* is warmed with a small flame in such a manner that bubbles of gas are slowly and uniformly evolved. When after boiling, for some time, the evolution of gas ceases and the liquid in the tube *a* begins to suck back, the flame is removed for an instant from the flask *k*, an aspirator connected to *e*, the tap of the dropping-funnel *z* opened, and air drawn slowly through the apparatus until all the carbon dioxide has been removed; this takes about half an hour. Whilst air is being drawn through the apparatus, the contents of the flask *k* may be kept gently boiling by means of a small flame, in order to assist the expulsion of the carbon dioxide from the flask and condenser, care being taken that the condensation is efficient. The tubes *c* and *d*, which are provided with glass stopcocks, are removed at the end of the determination, closed, placed aside for half an hour, opened momentarily, closed, and weighed.

Volatile organic compounds behave similarly to carbon dioxide, and are not condensed with the water-vapour; should they be present, therefore, too little organic carbon would be found. In such cases the pre-formed carbon dioxide and the organic carbon are determined together, by the initial addition of sulphuric acid, permanganate and mercuric sulphate. The pre-formed carbon dioxide is then determined separately in an equal volume of water and the organic carbon found by difference.

*B. Organic Carbon in the Suspended Matter.* The residue left on the filter from the filtration of the sample is treated together with the asbestos filter, in the flask *k*, Fig. 195, which in this case is of about 250 c.c. capacity, with 10 c.c. of 20 per cent. mercuric sulphate solution, and 5 g. of chromic acid or 10 c.c. of a 50 per cent. chromic acid solution, and the flask connected with the condenser and the absorption tubes; 50 c.c. of concentrated sulphuric acid are then added through the dropping-funnel.

*k*, a good flow of water being meanwhile maintained in the condenser, and the flask warmed, at first with a very small, and finally with a large flame, until no more gas passes through the Peligot tube. An aspirator is then attached, a slow current of air drawn through, and the determination continued as described under *A*.

Should the suspended matter contain calcium or magnesium carbonate, it must be boiled with dilute sulphuric acid before adding the chromic acid.

#### 14. Carbonic Acid.

The determination of pre-formed carbon dioxide may be carried out according to J. König's method as described under 14. In this case, the flask *k*, Fig. 195, is connected through the condenser with the absorption tubes from the start, and the tubes *c* and *d* are weighed before and after the decomposition with sulphuric acid only.

The qualitative detection and quantitative estimation of carbon dioxide, and also of free and half-combined carbon dioxide, are carried out as described under "Drinking Water and Water Supplies," p. 762.

#### 15. Detection of Excreta.

Animal excreta and products of animal and vegetable decay always contain small quantities of phenol, cresol, skatole, indole, and other compounds, which give intensely yellow coloured compounds with diazo-compounds, such as diazo-benzene sulphonic acid. P. Griess has based the following method for detecting the above-mentioned substances on this reaction: 100 c.c. of the water are treated in a cylinder of colourless glass with a little sodium hydroxide solution and a few drops of a freshly prepared solution of diazo-benzene sulphonic acid; if animal or vegetable products of excretion or decay are present, a yellow coloration appears within five minutes. For comparison, 100 c.c. of distilled water are similarly treated. Human urine is said to give a distinct yellow coloration at a dilution of 1 in 5000, and horses' urine at a dilution of 1 in 50,000.

To detect urea, which is, however, only present in very fresh effluents, 100 c.c. of the liquid are boiled with a few drops of acetic acid, filtered, evaporated to dryness, extracted with alcohol, the alcohol evaporated off, the residue dissolved in water, the solution evaporated down to 3 c.c. and then acidified with nitric acid; if urea is present twin-crystals of urea nitrate are formed on evaporation.

Dung particles may be detected in the sediment of a water by microscopic examination.

A simple test for recent faecal pollution is to warm a few c.c. of the liquid with an equal volume of strong sulphuric acid; a pink coloration indicates skatole.

In by far the greater number of cases, however, it is not possible to

directly detect these products of excretion and decay, and pollution from these sources can only be deduced indirectly from the presence of a large amount of nitrogenous organic matter (or, as this is easily decomposed, of nitric acid), of sulphur or sulphates, and of carbon or carbonates. As such refuse is also rich in chlorides, the chlorine content affords a further guide as to their presence. Even if the water is found to contain a large amount of any one of these substances this may be caused by the natural conditions; but if these compounds are present simultaneously in large amount, it is safe to conclude that pollution has occurred, especially if they are not contained to the same extent in other waters from the same locality.

#### 16. Detection of Coal Gas Products.

Contamination with coal gas products may occur through leakage from the mains. They are detected, according to C. Himly, by mixing a large quantity of the water with chlorine water, exposing the mixture to sunlight, and removing the excess of chlorine by agitation with mercuric oxide; if coal gas is present a strong smell of ethylene dichloride or of similar chlorinated hydrocarbons is observed. H. Vohl infers pollution by gas or tar water from the presence of ammonium sulphide or of ammonium carbonate, sulphate and thiosulphate, or from increased amounts of the corresponding calcium and magnesium salts. Phenol should also be tested for; if present, a violet coloration is produced by ferric chloride, a yellowish-white precipitate of tribromophenol bromide by bromine, and rosolic acid is formed on heating with oxalic and sulphuric acids. It is also advisable to test for thiocyanates with ferric chloride, as these are present in ammonia recovery liquor, which is often discharged into the sewers.

#### 17. Tests for Putrescibility: Fermentation Experiments on Effluents.

The view that a water which keeps clear for five or more days without undergoing putrefaction is fit for distribution does not always hold good. For instance, a perfectly clear water may be prepared by the addition of an excess of lime which may be kept for a long time in well-closed bottles without putrefactive bacteria making their appearance, as free lime hinders their development. If the same liquid is kept in open vessels the free lime is gradually neutralised by carbon dioxide, and putrefactive bacteria then appear and decompose the soluble organic matter, but without producing any smell of putrefaction. If, however, a similar effluent containing a large amount of free lime flows into a slow-flowing river, the formation of mud is not improbable, and in this case unpleasant smells may be produced, especially in warm weather.



Although, therefore, tests on the putrescibility of effluents have usually little practical bearing, they sometimes allow of conclusions as to the greater or lesser capability of decay of the contained organic matter, and consequently in regard to the degree of harmfulness of the effluent.

The following methods are adopted in testing the putrescibility of water :—

(a) Two bottles, each containing  $\frac{1}{2}$  to 1 litre of the water, are allowed to stand uncovered.

(b) Two bottles, containing the same quantities as in a, are closed with sterilised cotton-wool.

(c) Two bottles, also containing the same quantities, are kept well-stoppered.

One of each of these pairs of bottles is kept at a low temperature,  $0^{\circ}$  to  $10^{\circ}$ , and the other at  $10^{\circ}$  to  $20^{\circ}$ .

If the water contains free lime, a further pair of bottles is filled with the sample, in which the lime has been previously neutralised with carbon dioxide, and is then treated in the same manner as the others.

If it is necessary to dilute the water, this is done with distilled water which has been boiled for some time and then cooled, the vessel being meanwhile closed with a plug of cotton-wool.

If the effluent contains no putrefactive bacteria, a further series of bottles are equally inoculated with any liquid which is in a state of putrefactive fermentation.

The separate samples are then examined after a fixed time, microscopically, bacteriologically, and also chemically, for ammonia, nitrous acid, hydrogen sulphide, oxygen-absorbing power with permanganate, total nitrogen, colour, smell, etc.

The incubator test described on p. 816 may also be employed, or a mixture of one volume of the sample with say nine volumes of tap-water is submitted to incubation in a completely filled and closed bottle for several days, and the loss of oxygen noted. (Cf. also Adeney's experiments, p. 786.)

## MICROSCOPIC AND BACTERIOLOGICAL EXAMINATION

The microscopic and bacteriological examination of effluents is essentially the same as that of drinking water. (Cf. p. 789.) The occurrence of *Beggiatoa* and of *Leptomitus* demand special attention in the case of effluents containing more or less albuminoid matter, such as those of breweries, sugar-, starch-, and paper-factories, etc. *Beggiatoa* occurs under the inflow of effluents into brooks and rivers in thick

slimy beds which cover stones, wood, and other materials in the water; they are composed of countless, fine, non-branching threads which, in the riper stages of development, contain varying quantities of embedded, sulphur-coloured grains. Alcoholic solutions of aniline dyestuffs, sodium sulphite, etc., show up the structure of the threads, which are articulated into long and short rods and, in older threads, into discs and coecæ. The fungus *Leptomitius lacteus* covers the bed of the stream with a greyish-white slime; it differs from *Beggiatoa* by the threads showing both branches and constrictions.

### CRITERIA AS TO THE CONTAMINATION DUE TO EFFLUENTS AND THEIR INJURIOUS EFFECTS

In examining the contamination of a stream due to the effluents from a works or factory, the sample must be collected at the point where a possible injurious effect is suspected, as otherwise, in consequence of self-purification, the water may subsequently lose its specific deleterious character. The use for which the water in question is destined must also be borne in mind, because the injurious effects of the constituents of effluents act harmfully in very various ways according as to whether the water is employed for fish-culture, drinking-supply for cattle, industrial purposes, agricultural purposes (for soil and vegetation), etc.; accordingly a water which is injurious for one purpose may be quite harmless for another.

#### 1. Effects on Fish-culture. . .

The fact that fish have died in a stream polluted by an effluent cannot in itself be considered as a proof of the injurious character of the effluent in question, as observations of extensive illness or mortality amongst fish are on record which were due to natural diseases and not to effluent pollution. The following methods are available for determining the injurious effect of an effluent or of the water of a stream contaminated thereby.

A. *By Examination of the Fauna and Flora of the Contaminated Water.* Natural waters in which fish are to live must contain a sufficient quantity of animals and plants for their food. According to the degree and character of the contamination, the animal and vegetable life of the water may either be totally destroyed, or its development hindered, or it may be changed in character. Comparison with neighbouring parts of the same waters, of as similar a character as possible but not liable to contamination from the same source, may considerably simplify the investigation in this respect. More specific inquiries on this aspect of the pollution necessitate an expert zoological and botanical examination.

*B. By Examination of the Fish.* When the water is contaminated by either copper, zinc, lead, iron, arsenic, or dyestuffs, etc., an examination of the fish may prove helpful. Fish sent for examination should be wrapped singly in parchment paper and packed in ice and straw. Either the whole fish, or the flesh and the intestines separately, are tested for the suspected injurious substances by the ordinary toxicological methods.

*C. By Examination of the Water and by Experiments on its injurious Effect on Fish.* The examination of the water is especially necessary when several effluents of varying character participate in the contamination, or when the constituents of the effluent alter on standing. Effluents which contain large amounts of organic matter, such as town effluents and effluents containing fæces, may be quite harmless to fish when fresh, and in fact some fish often frequent, by preference, the places where such effluents enter the stream; when, however, the organic matter of such effluents putrefies, the water may become injurious to fish in consequence of deficiency of oxygen, or of the formation of hydrogen sulphide, ammonia, etc. The limiting figures which have been found by experiment for the individual injurious constituents cannot, and should not, be considered as applicable in all cases, but only as giving a general idea. C. Weigelt<sup>1</sup> has called attention to the fact that not only are the various species of fish affected differently by any one harmful ingredient, but also that the effect varies with the same species when of different weight and age. The temperature has also an influence, the harmful effect of any ingredient usually rising and falling with the same. In many cases, it is not possible to come to any final conclusion from the recorded results for the limiting amounts of the individual injurious constituents, and it is then necessary to make direct experiments, either with the contaminated water or with the contaminating substances.

The following limiting quantities for various harmful substances were obtained by Haselhoff<sup>2</sup> as the result of direct experiments at the experimental station at Münster. The experiments were performed with carp, tench, and goldfish; the figures always refer to 1 litre of water, and indicate, unless otherwise noted, the point at which the fish became ill or died.

1. *Oxygen Content*: Fish thrive unharmed on 2.8 c.c., i.e. about  $\frac{1}{3}$  of the amount of oxygen usually present in flowing water. The effect of a deficiency of oxygen in putrefying water is associated with other changes, including the formation of the substances 2 to 5, which may have an injurious effect.

2. *Hydrogen Sulphide*: 8 to 12 mg.

<sup>1</sup> *Landw. Versuchsst.*, 28, 321; *Archiv f. Hyg.*, 1885, 3, 39.

<sup>2</sup> *Landw. Jahrbuch*, 1898, 26, 115; 1897, 25, 182.

3. *Free Carbon Dioxide*: 190 to 200 mg.
4. *Free Ammonia*: 17 mg. for small, and 30 mg. for large fish.
5. *Ammonium Carbonate*: 170 to 180 mg.  $(\text{NH}_4)_2\text{CO}_3 + 2\text{NH}_4\cdot\text{HCO}_3$   
= 36 to 38 mg. ammonia.
6. *Ammonium Chloride*: 0.7 to 1.0 g.
7. *Ammonium Sulphate*: 0.7 to 1.0 g.
8. *Sodium Chloride*: 15 g.
9. *Sodium Carbonate*: 5 g.
10. *Calcium Chloride*: 8 g.
11. *Magnesium Chloride*: 7 to 8 g.
12. *Strontium Chloride*: 145 to 172 mg.; this limit can be raised to 181 to 235 mg. if the quantity added to the water is increased gradually.
13. *Barium Chloride*: In individual cases 20.3 mg. acted injuriously, whereas in others 64.3 to 500 mg. produced no effect; fish seem to be very variously affected by barium chloride and to be able to accustom themselves to it to a certain degree.
14. *Zinc Sulphate*: 31 mg.  $\text{ZnO} = 110$  mg.  $\text{ZnSO}_4$ . The fine, flocculent zinc hydroxide which is separated exerts an additional injurious effect by settling on the gills and affecting respiration.
15. *Copper Sulphate*: 4 mg.  $\text{CuO} = 8$  mg.  $\text{CuSO}_4$ ; smaller amounts may act injuriously in course of time.
16. *Ferrous and Ferric Sulphates*: The injurious action of these salts varies with the amount of flocculent ferric hydroxide which separates; the experiments showed an injurious effect with 40 to 50 mg. of ferrous sulphate. C. Weigelt observed no injurious effect with 50 mg. of ferrous sulphate, but found that 15 to 30 mg. of ferric sulphate was deleterious.
17. *Free Lime*: 23 mg.  $\text{CaO}$ .
18. *Free Sulphuric Acid*: 35 to 50 mg.  $\text{SO}_3$ .
19. *Sulphurous Acid*: 20 to 30 mg.
20. *Free Hydrochloric Acid*: 50 mg.
21. *Potassium Alum*: 300 mg.  $\text{K}_2\text{Al}_2(\text{SO}_4)_4 + 24\text{H}_2\text{O}$ .
22. *Chrome Alum*: 230 mg.  $\text{K}_2\text{Cr}_2(\text{SO}_4)_4 + 24\text{H}_2\text{O}$ .

A number of different dyestuffs were also investigated with regard to their deleterious action on fish.<sup>1</sup>

## 2. Injurious Effect on Live Stock.

As pure water should be demanded for cattle as for human beings, although cattle may be less susceptible to the injurious effects of impurities in the water. In the case of milch cows in particular impurities in the drinking-water may act injuriously, as the composition of the milk may be adversely affected; abortion may be caused in the

<sup>1</sup> Cf. *Landw. Jahrb.*, 1901, 30, 583.

case of pregnant animals through pollution of the drinking-water with putrid matter or with purgative salts such as chlorides, sulphates, or nitrates, in considerable quantity; horses may develop colic from the same causes, etc.

Water contaminated by effluents containing poisonous substances such as lead, copper, zinc, arsenic, etc., may spoil herbage when meadows or fields are flooded, either by mechanical adhesion of these impurities to the plants or by absorption; in either case the health of the stock consuming such fodder may be injuriously affected. Poisons of this character are detected in the fæces, and under certain circumstances in the urine; in the case of dead animals, in the remains of food in the stomach and intestines.

### 3. Injurious Effect for Industrial Purposes.

Any water which is turbid or which is strongly contaminated by sludge, dyestuffs, or mineral matter, must be rejected for industrial and technical purposes.

In the case of feed water for boilers it is necessary to distinguish between substances which actually attack and destroy the boiler plates, and those which cause the formation of boiler-incrustation and thus hinder the conduction of heat. To the first category belong free acids, ammonium salts, magnesium chloride, much dissolved oxygen, humus substances, and grease (from machine oils); molasses have also been found to be injurious to the boilers in sugar-factories. According to the investigations of Fischer, the formation of boiler-scale is to be specially attributed to the presence of calcium sulphate, calcium carbonate, and magnesium carbonate. This question is fully dealt with in the section on "Feed Water for Boilers and Water for other Technical Purposes," p. 799.

Water for paper mills, dye-works, print-works, bleach-works, and glue-works, must be soft and especially free from iron.

Sulphates, alkali carbonates, and especially nitrates, actively assist the formation of molasses, and waters containing these substances cannot therefore be used in sugar-works.

In all fermentation industries, especially breweries and distilleries, perfectly pure, clear, and soft water is required. The water must, above all things, be free from products of decay, and must contain as few micro-organisms as possible, as these cause subsidiary fermentations which may adversely affect the aroma and taste of the products.

Such water must also be rejected for use in dairies, as vessels cleaned with it would retain micro-organisms and injuriously affect the separation of curd; also, butter which has been washed with such water would soon become rancid and bad.

## INJURIOUS EFFECTS OF EFFLUENTS

### 4. Injurious Effect on the Soil.

An effluent, or a brook contaminated by an effluent, may affect the soil injuriously in three ways. If the water contains much suspended matter, such as iron oxide mud, particles of cinder, slag, or charcoal, organic fibres, etc., these substances may clog the soil, either by forming a thick layer on the surface and choking the normal vegetation, or by stopping up the pores in the soil, thereby causing it to become acid, and thus injuriously affecting the vegetation.

An effluent may also convey substances to the soil which are either directly injurious to plants, such as ammonium thiocyanate, arsenious acid, metallic oxides, etc., or which are converted by oxidation into injurious substances—for instance, sulphur compounds.

Finally, free mineral acids, chlorides of sodium, calcium and magnesium, and ferrous, copper, and zinc sulphates and nitrates, exert a solvent action on the constituents of the soil, when carried to meadows or fields by an effluent, so that after they have acted for some time the soil becomes steadily poorer in calcium, magnesium, and potassium, and, after a longer or shorter period, according to the original fertility, the crops become poorer. In consequence of this solvent action on nutrient constituents, the productiveness of the soil may at first be actually improved; hence it is often concluded that such waters are not harmful, but both practical experience and scientific investigations have fully established the harmful effect of such effluents. In the case of the sulphates the corresponding metallic oxide remains behind in the soil and may be absorbed by the plants. The chlorides, moreover, effect a closer juxtaposition of the soil particles, which makes the ground heavy and therefore less fertile.

In determining whether a soil has suffered injury from effluents, it is therefore necessary, not only to estimate the amount of the injurious substance in the soil and in the vegetation growing on it, but also the contained calcium, magnesium, and potassium, and the degree of juxtaposition of the soil particles, in comparison with those of a similar soil which has not been affected by the effluent. In certain cases the action of a certain type of effluent is indicated by the character of the vegetation; for instance, the occurrence of *Arabis Halleri* or *Petraea* is characteristic for soils which have been damaged by zinc compounds, and *Atriplex hastata* for those which have been spoilt by common salt.

The sampling and examination of the soil is carried out as described in the section on "Soils," p. 841.

### 5. Injurious Effect on Plants.

The action of injurious effluents on plants cannot always be proved by an examination of the plants themselves, as some injurious substances,

such as ammonium thiocyanate, very soon undergo change by vegetable metabolism. Other injurious substances, such as arsenious oxide, are only absorbed in very minute amount, but a large number, especially metallic chlorides and sulphates, are absorbed by the plants in considerable quantities.

#### 6. Injurious Action on Ground- and Well-Waters.

If the composition of a ground- and well-water has been affected by an effluent soaking into the soil, the characteristic constituents of the effluent, or the products of their interaction with the constituents of the soil, should be capable of detection in the water. In cases of this character it is advisable to also collect samples of the ground-water along the line of communication between the source of contamination and the contaminated well, as the examination of such samples may be helpful in drawing conclusions with regard to any effect of the effluent on the well-water.

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## SOILS

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SOILS are divided into two main classes, mineral soils and peat or "moor" soils, according to their origin, quality, and agricultural treatment; the first class is characterised by containing a predominant proportion of mineral constituents, whilst soils of the second class consist mainly of organic matter.

The two classes differ so widely in composition and in their properties and behaviour that different methods must be employed for their examination.<sup>1</sup> As an outcome of the view expressed by Liebig, that plants derive their nourishment from the air and the soil, and that they could only grow on a soil which contained the constituents of their ash, it was concluded that in order to examine the fertility of a soil it was only necessary to determine chemically how much it contained of the various constituents absorbed by plants; as consequence special attention was devoted to soil analysis. It was soon found, however, that the importance of chemical analysis had been exaggerated, and that the fertility of a soil depended not only on the amount of plant food present, but also on other factors, especially the mechanical and physical condition of the soils, which have since become an important feature in their examination. At the same time, the chemical analysis of soil leads to valuable conclusions, more especially when employed in conjunction with field experiments.

The nutrient constituents of soils are present in very different states of solubility; hence the analytical results depend very largely on the nature of the solvent which is used. A uniform method of procedure is therefore essential if the results of soil analyses are to be directly comparable with one another.<sup>2</sup> According to F. Wahnschaffe the

<sup>1</sup> The description of the methods employed in the examination of peat or "moor" soils (Moorboden) given in the German edition, Vol. I., pp. 905-908, has been omitted from the translation, as agricultural soils of this character are rarely worked either in Great Britain or in the British Colonies.

<sup>2</sup> The methods given in the German edition are based on those agreed to by the Union of Agricultural Experimental Stations of the German Empire.



following points should be considered in the examination of soils; it is to be understood, however, that it is not always necessary to carry out all the methods of investigation involved.

1. *The general Profile of the Soil*, so far down as it is of any importance to vegetation, should be indicated, especially the thickness of the soil proper, and of the immediate and the final subsoil.

2. *Mechanical Analysis*. All three layers should, as far as possible, be subjected to mechanical analysis (the surface soil always, except in the case of peat or "moor" soil), as knowledge is thus gained with regard to the physical properties and degree of intermixture of the soil.

3. *Examination of the Subsoil*. The determination of calcium carbonate and of clay is important.

4. *Amelioration*. If the layers of subsoil are to be used for purposes of amelioration they must be examined for constituents useful and harmful to vegetation; the former comprise chiefly calcium carbonate and phosphoric acid, the latter ferrous sulphate, free sulphuric acid, and iron sulphide.

5. *Surface Soil*. In all chemical and physical examinations of the surface soil, the fine earth (under 2 mm. diameter), dried at  $105^{\circ}$ , should be used, and all results expressed with regard to the same.

6. *Separation of the Constituents of the Soil*. The quantities of calcium carbonate, clay, humus, and sand are determined in the fine earth of the surface soil, dried at  $105^{\circ}$ .

7. *Nitrogen*. The determination of nitrogen is carried out in the surface soil only, except in the case of moorland soils.

8. *Nutrient Constituents*. The extract with boiling concentrated hydrochloric acid is to be used for the determination of the nutrient constituents. Of these, calcium, magnesium, potassium, phosphoric and sulphuric acids are the most important; silica, alumina, sodium carbonate and the oxides of iron, and manganese are only of secondary importance.

9. *Available Nutrient Constituents*. For the determination of the "available" phosphoric acid and potash, a solution containing 1 per cent. of citric acid as proposed by B. Dyer<sup>1</sup> is almost universally employed.<sup>2</sup> In the United States the use of  $N/5$  and  $N/200$  hydrochloric acid has been extensively adopted. In Germany the potash is extracted with lime-water, and the phosphoric acid with either citric or acetic acid.

10. *Knop's Absorption Coefficient*. This determination is only carried out with the surface soil.

11. *Physical Examination*. The most important physical determinations are the water-capacity, which should if possible be made on the spot, the capillarity, and the evolution of heat on moistening.

<sup>1</sup> *J. Chem. Soc.*, 1894, 65, 115.

<sup>2</sup> *Cf. Hall and Plymen, ibid.*, 1902, 81, 117.

## I. SAMPLING

Provided that the nature of the soil is fairly uniform, samples are taken in 3, 5, 9, 12, or more different places, according to the area, at uniform distances from one another. The samples are obtained by vertical cuts of uniform depth, equal to that turned by a plough. If the subsoil is to be examined the samples must be taken down to a depth of 60 or 90 cm. The samples are either examined separately, or, if an average value is required, they are carefully mixed, and a suitable quantity taken for analysis.

Samples are conveniently taken either with a worm or with a cylindrical auger.

In England it has been customary to take all soil samples down to a depth of 9 inches (22.8 cm.), unless the preliminary examination of the soil profile shows a sharp change from soil to subsoil before that depth is reached.

At Rothamsted, where the soil contains a large proportion of flint stones, a rectangular steel frame, 9 inches deep and 6 inches square, is employed to take samples. The frame is about half an inch thick in the metal and tapers off to a chisel edge below. The ground is raked smooth if necessary, the frame placed on it and driven down by means of a heavy wooden rammer until the upper edge is flush with the soil. The contents of the frame are then carefully picked out and placed in a closed case of tinned iron for removal to the laboratory and weighing. To obtain a second depth of 9 inches, a wooden cover is then put on the frame and the surrounding soil removed down to the depth of 9 inches. The cover is then taken away, the frame driven into the soil as before, and the contents removed. These processes are repeated for as many depths as may be desired.

The auger method of sampling fails if the ground contains many stones, and becomes practically impossible after continued dry weather. A convenient tool consists of a steel cylinder 2 inches in diameter and 12 inches long, with a vertical slot about three-quarters of an inch broad, the lower edge of the cylinder and the edges of the slot being sharpened.<sup>1</sup>

For a complete examination at least from 4 to 5 kilos of soil should be taken and dried, either in the air or in a drying oven, at 30° to 40°, care being taken to protect the sample from dust, etc.

Notes should be taken on the following points in sampling:—

A. The geological origin of the soil.

B. The depth of the surface soil, the condition of the subsoil immediately below it, and, as far as possible, the nature of the lower layers. It is also desirable to indicate whether the soil is derived from

<sup>1</sup> Cf. A. D. Hall, *The Soil*, p. 45.

the geological formation underlying it, in which case it may be described as a "sedentary" soil, or whether it is a "soil of transport" or "drift" soil. In the latter case, if the thickness of the "drift" be small, it is necessary to know the nature of the underlying "solid" formation, but when, as in many places in the Midlands and in the North of England, the drift is of glacial origin and is 50 feet or more in thickness, the "solid" geology is unimportant as far as the soil is concerned.

C. The climatic conditions, especially the height above sea-level.

D. The method of cultivation and the sequence of crops in previous years.

E. The nature and quantity of manure used.

F. The yield of the crops obtained in previous years, and, if possible, the average yields of the area in question when growing the more important crops.

G. The practical valuation of the soil, its nature, fertility, etc.

H. The depth of ground-water, the slope and aspect of the soil, etc.

Larger stones and pebbles are separated from the air-dried soil by sieving, rinsed with water, and their mineralogical character, weight, and approximate size determined.

## II. MECHANICAL EXAMINATION

The object of the mechanical analysis of soil is to determine quantitatively the relative amounts of the coarser and finer constituents. This knowledge is of importance for the following reasons. The finest material, or clay portion, of the soil is, from a chemical standpoint, the fertile element, as it contains all the nutrient substances in a concentrated form and accessible to the roots of the plant. On the other hand, its physical character is unfavourable, as it is impermeable to water and, after drying, also to air; further, it is capable of absorbing very large quantities of water, whereby its volume undergoes considerable change, either when water is taken up or given off. These characteristics of the finest particles, which are unfavourable to fertility, can be modified or completely neutralised by admixture with the coarser material.

In the mechanical analysis of soil those portions of a coarseness greater than 2 to 3 mm. diameter, are determined by means of sieves of 2 to 3 mm. mesh, the finer portions by elutriation.

J. Kühn<sup>1</sup> recommends the following method for the estimation. The sample, which should be as fresh as possible, is first broken up so that only stones remain behind, on subsequently passing the sample through a sieve of 5 mm. mesh. It is then spread out uniformly in a suitable place, free from dust, until air-dry, weighed, and passed

<sup>1</sup> *Landw. Versuchsst.*, 1893, 42, 153.

through a 5 mm. sieve. The stones remaining in the sieve are freed from adherent earth by washing with water, weighed when air-dry, and their weight expressed as a percentage of the total soil.

The soil which has passed through the 5 mm. sieve consists of coarser mineral fragments and of fine earth ( $<2$  mm.). Note should be taken whether the coarser portions consist of water-worn pebbles or of fragments of rock disintegrated *in situ*. The various portions are further designated as follows:—

	Size of Grain. Diameter in mm.	Designation.
	Over 5	Stones.
	Between 5 and 2	Gravel.
Fine Earth	„ 2 „ 1	Very coarse sand.
	„ 1 „ 0.5	Coarse sand.
	„ 0.5 „ 0.2	Medium sand.
	Below 0.2	Fine sand.
	Elutriable portion	{ Very fine sand, mineral dust, clay, etc.

The elutriable portions must be examined microscopically for larger and smaller quartz particles, mica, clay particles, etc.

For the analysis, 50 g. of the dust-free soil which has passed through the 5 mm. sieve are taken if it is of fine texture, 100 g. if it contains much coarser material, and gently boiled with 500 c.c. of water in a porcelain dish, with frequent stirring with a spatula, until all earth particles are thoroughly broken up. The whole is then passed through a 2 mm. sieve into a Kühn elutriating cylinder; the residue remaining on the sieve is rinsed thoroughly above the cylinder and dried in the air. It is then separated by means of a 3 mm. sieve into coarse gravel (5 to 3 mm.) and fine gravel (3 to 2 mm.) and each part weighed separately.

As no general agreement has been come to with regard to the definition of the term “fine earth,” the size of grain of the fine earth used in an analysis should be stated.

It has been agreed in this country<sup>1</sup> to reckon as fine earth for analysis, the material which passes through a sieve with round holes of 3 mm. diameter.

At Rothamsted, however, a woven wire sieve with meshes of  $\frac{1}{4}$  inch diameter (6.35 mm.) has always been used; this passes a little more than the 3 mm. round-holed sieve.

The fine earth is further separated by elutriation. The forms of apparatus used for this purpose effect the separation of the various portions, either by means of their different rates of fall in still water, or by means of an ascending stream of water; the former method is adopted

<sup>1</sup> Cf. *Analyst*, 1900, 25, 281.

in Kühn's apparatus, the latter in that devised by Schöne, which has already been described in the section on "Calcareous Cements," p. 690.

Kühn's elutriating apparatus consists of a glass cylinder 30 cm. high and of 8.5 cm. internal diameter; the lower end is furnished with a side tube of 1.5 cm. diameter, and is closed with a rubber stopper which is fixed at a height of 5 cm. from the bottom of the cylinder.

To carry out a determination, the fine earth is placed in the cylinder, water added up to the mark, which is 2 cm. below the rim, and the whole thoroughly stirred up for one minute with a smooth wooden rod. The rod is then removed, drained into the cylinder, and the whole allowed to stand quietly for ten minutes. The stopper of the side tube is then taken out and the turbid water run off, a sample being collected in a test-tube. These operations are repeated until, after standing for ten minutes, no suspended particles can be observed above the side tube; care must be taken that the end of the stopper of the side tube is always placed flush with the inner wall of the cylinder. A test-tube sample is kept from each operation and the various portions are united in a beaker, filtered, the residue thoroughly mixed and used for the microscopic examination.

The sand remaining in the elutriation cylinder is rinsed into a porcelain dish, dried on the water-bath, and allowed to stand in the air in a dust-free place for twenty-four hours, to attract hygroscopic moisture, after which it is weighed. It is then passed successively through 1 mm., 0.5 mm., and 0.25 mm. sieves, in order to obtain the weight of "very coarse sand" (2 to 1 mm.), "coarse sand" (1 to 0.5 mm.), "fine sand" (0.5 to 0.25 mm.), and "very fine sand" ( $< 0.25$  mm.). Any loss, on the original weight, caused through dusting whilst sieving, is reckoned as "very fine sand." The weights found are calculated to percentages on the pebble-free, air-dried soil, and the proportion of elutriable material taken by difference.

The data thus obtained should always be accompanied by a microscopic examination, and the proportion of quartz particles to the finer constituents in the elutriable portion of the fine earth should also be determined.

The various methods of mechanical analysis of soils have been subjected to a critical examination by Osborne,<sup>1</sup> who obtained satisfactory agreement between a method similar to that of Kühn, depending upon suspension for given intervals of time in beakers and the running-water method of Schöne, as improved by Hilgard.<sup>2</sup> One difficulty common to all methods is the initial resolution of the soil into its ultimate particles either by boiling or by rubbing up with water.

<sup>1</sup> *Connecticut Agricultural Experimental Station Reports*, 1886 and 1887; cf. also, Wiley, *Principles and Practice of Agricultural Analysis*, 2nd ed., vol. i., p. 260.

<sup>2</sup> *Amer. J. Soc.*, 1873, 6, 288.

Schlösing<sup>1</sup> introduced the plan of a preliminary treatment with weak acid followed by ammonia in order to dissolve the humus, which acts as a cement and binds some of the finer particles into loose aggregates. This procedure has been justified by Hall,<sup>2</sup> and is now generally adopted by analysts in this country.

The whole method is carried out as follows:—Two portions, one A, of 100 g., the other B, of 10 g., of the air-dried fine earth, are weighed out. The smaller portion, B, is placed in a porcelain dish with 100 c.c. of  $N/5$  hydrochloric acid and gently rubbed up with a soft pestle, made by fixing a rubber bung on the end of a glass rod. The soil is left in contact with the acid for an hour, and is then transferred to a filter and washed until free from acid, which state is indicated as soon as the filtrate begins to show any turbidity. Meanwhile, a beaker with a lip (9.5 cm. high and 8 cm. diameter is a convenient size) is got ready by making two horizontal marks on the side, at 8.5 and 7.5 cm. from the bottom respectively. The soil is washed into this beaker through a sieve made of No. 100 brass wire-cloth, 100 meshes to the inch, until the residue on the sieve is clean. The sieve and its contents are then dried, the material retained by the sieve, which is all  $> 0.2$  mm., is brushed out into a tared capsule, dried in the steam-oven, and weighed.

To the material in the beaker (particles  $< 0.2$  mm.), 1 or 2 c.c. of strong ammonia are added, and the whole carefully rubbed up with the soft pestle. The beaker is then filled up to the 8.5 cm. mark, covered over to keep out dust, put aside, and allowed to stand undisturbed for twenty-four hours. After this interval the supernatant turbid liquid is poured off, a few c.c. of ammonia added as before, the rubbing with the soft pestle repeated, water added to the mark, and the whole again put aside for twenty-four hours. This process is repeated on successive days until the supernatant liquid remains practically clear for the twenty-four hours. The turbid liquid poured off contains all the particles below 0.002 mm. in diameter, reckoned as clay (or "klay," to distinguish it from the loosely applied common term). The various portions of "klay" water may be all united, well shaken, measured, and an aliquot portion evaporated to dryness and weighed to obtain the weight of the "klay" fraction. It is perhaps more convenient to put aside a porcelain basin in which the "klay" water is evaporated each day, so that the whole of the "klay" is collected in one basin and can be dried in the oven and weighed. Water is then added to the sediment in the original beaker, from which the "klay" particles have been removed, up to the 7.5 cm. mark, the whole well stirred, allowed to stand for twelve and a half minutes, and the turbid liquid poured off as before, the operation being repeated until nothing appreciable remains floating for twelve and a half minutes. The turbid liquid poured off

<sup>1</sup> *Comptes rend.*, 1874, 78, 1276.

<sup>2</sup> *J. Chem. Soc.*, 1904, 85, 950.

contains only particles  $> 0.002$  mm. but  $< 0.01$  mm. diameter. It may be either evaporated and the residue weighed, or put aside until the whole of the sediment has deposited, the bulk of the liquid decanted off, and the residue only washed into a capsule for evaporation and weighing in the dry state.

Finally, the sediment still remaining in the beaker is again divided into two fractions by the same method, filling up to the 7.5 cm. mark, and using a time interval of seventy-five seconds only. By this means the 10 g. of soil are divided into a fraction arrested by the sieve, and fractions capable of remaining suspended in the beaker for twenty-four hours, twelve and a half minutes, seventy-five seconds, and less than seventy-five seconds respectively.

Owing to the difficulty of drawing a sample weighing only 10 g. that shall have the coarser particles fairly distributed in it, the other sample of the soil weighing 100 g. is treated with acid as described above. The soil is then thrown upon a tared filter paper, washed until free from acid, and the residue weighed to ascertain the loss by solution. It is then passed successively through two sieves, the first with round holes 1 mm. in diameter, the second a woven wire sieve as described above. The fractions arrested by each sieve are weighed and taken to show the true percentages of particles  $> 1$  mm. and between 1 mm. and 0.2 mm. in diameter respectively. The proportions of the finer grades are re-calculated, if necessary, to allow for the somewhat erroneous proportion of material arrested by the sieve which will have been found in dealing with the 10 g. sample only. To complete the analysis, a determination of the moisture in a sample of the original soil is also needed. The data thus obtained are as follows:—

<i>Fine Gravel</i> , 3 mm. to 1 mm. diameter.	}	Separated by sieves.
<i>Coarse Sand</i> , 1 mm. to 0.2 mm.        "		
<i>Fine Sand</i> , 0.2 mm. to 0.04 mm.       "	}	Separated by sedimentation.
<i>Silt</i> , 0.04 mm. to 0.01 mm.       "		
<i>Fine Silt</i> , 0.1 mm. to 0.002 mm.       "		
" <i>Klay</i> ," below 0.002 mm.       "		
<i>Material soluble in dilute acid.</i>		
<i>Hygroscopic Moisture.</i>		

### III. PHYSICAL EXAMINATION

The physical examination of soils is rendered difficult by the fact that it is impossible to examine them in the laboratory with their various portions in the same relative order as they occur in nature. This very considerably depreciates the practical value of the results obtained, and on this account the physical properties of soils are but

seldom determined; the following are the most important physical methods of examination:—

**Determination of Capillary Attraction.**—The capillary attraction or lifting power for water of soil is very closely connected with its mechanical composition; the finer the constituents the larger is the number of capillary cavities, and consequently the greater the capillarity. The fertility of soil is essentially dependent upon the amount of water held by capillary attraction, whilst any excess of ground-soil water is disadvantageous to vegetation; the latter must therefore be removed by drainage. The capillary attraction is determined in glass tubes 100 cm. long and of 2 cm. internal diameter, graduated in cm.; the lower end of each tube is closed with a piece of muslin or fine linen, which is held in place by a rubber ring. The tubes are filled with air-dried fine earth, with gentle tapping, and are then placed vertically in a trough filled to a depth of 1 to 2 cm. with water; the time which the water takes to reach heights of 20, 30, 40, 50, 60, and 70 cm. is determined, and also the time in which the maximum height is reached. The water absorbed from the supply vessel must be continuously replaced.

**Determination of the Capacity for Water.**—The capacity for water of a soil is the amount of water which it can hold in its pores. A cylinder of sheet zinc or glass of 4 cm. internal diameter and of exactly 200 c.c. capacity, the bottom of which is closed with fine nickel-wire gauze, is used for the determination. A moistened linen disc is placed on the gauze and air-dried soil then introduced into the cylinder in small portions at a time, with gentle tapping on a soft surface, so that a firm and uniform mass of soil is obtained. The cylinder and soil are weighed and then placed in a trough of water so that the gauze bottom is 5 to 10 mm. below the surface. A bell-jar is placed over the cylinder to prevent access of air, and the water allowed to soak into the soil from below. After some time, varying with the nature of the soil, moisture will appear on the surface of the soil; the cylinder is kept in the water until the increase in weight is approximately constant, when the whole is again weighed and the weight of absorbed water thus determined.

An alternative and preferable method of determining the water capacity of soils has been devised by Hilgard.<sup>1</sup>

**Determination of the Absorptive Power for Salts in Solution.**—For this purpose solutions of the more important nutrient substances, such as ammonium chloride, potassium nitrate, calcium nitrate, magnesium sulphate, and acid calcium phosphate, containing  $\frac{1}{10}$  or  $\frac{1}{100}$  g. molecules per litre, are most suitable. The absorptive power for a

<sup>1</sup> *United States Department of Agriculture, Division of Chemistry, Bulletin, 38, 1893; cf. also, A. D. Hall, The Soil, pp. 64 and 76.*



complete nutrient solution is determined on a mixture made up of  $N/50$  solutions of potassium and calcium nitrates, magnesium sulphate, and acid calcium phosphate.

Air-dried soil which has been passed through a 0.5 mm. sieve is used for the determination. Fifty g. of the soil are allowed to stand with 200 c.c. of the solution to be examined, for forty-eight hours, in a tightly closed flask, at the ordinary temperature; the liquid is then poured on to a pleated filter paper, and the quantity of unabsorbed salt determined in the filtrate.

The filtration method proposed by W. Pillitz and N. Zalomanoff<sup>1</sup> is more in accordance with natural conditions. The apparatus consists of two cylinders placed vertically one above the other; the top of the lower cylinder and the bottom of the upper cylinder are each provided with a rubber stopper carrying a small glass tube, and the two tubes are connected by a piece of rubber tubing provided with a pinch-cock. The lower cylinder is graduated in c.c., and the opening of the connecting tube in the upper cylinder is closed with a disc of filter paper. A weighed quantity of the soil is placed in the upper cylinder, a measured volume of the solution added, the pinch-cock between the connecting tubes then opened, and a definite volume of the solution allowed to filter, drop by drop, through the soil. Both the liquid which has percolated and that remaining in the upper cylinder are stirred, and the quantity of dissolved salt remaining in both determined; the absorptive power is thus found by difference.

The term "Coefficient of Absorption" has been suggested by M. Fesca to express the amount of the absorbed constituent in mg. per 100 g. of soil.

According to Knop,<sup>2</sup> the absorptive capacity for ammonia is all that is required for the valuation of soil. F. Wahnschaffe has, however, rightly pointed out that it would be wrong to form an opinion of a soil from one favourable characteristic alone, which might be entirely neutralised by other unfavourable properties. Knop determines the absorptive power as follows:—Fifty g. of the soil, which has been passed through a  $\frac{1}{4}$  to  $\frac{1}{3}$  mm. sieve, is mixed with 5 g. of powdered chalk; this addition of chalk is especially necessary in the case of soils containing little lime, and serves to neutralise the hydrochloric acid liberated from ammonium chloride solution owing to the absorption of ammonia. The mixture of soil and chalk is digested for forty-eight hours, with frequent shaking, with 100 c.c. of an ammonium chloride solution containing 1 g. of ammonium chloride = 0.2619 g. nitrogen per 209 c.c.; on decomposition in the azotometer this solution yields 209 c.c. of nitrogen at 0° and 760 mm. pressure, so that 1 c.c. of the

<sup>1</sup> Cf. J. Kühn, *Berichte d. landw. Instituts. Halle*, 1880, 40.

<sup>2</sup> *Landw. Versuchsst.*, 17, 85.

solution corresponds to 1 c.c. of nitrogen gas. After digestion, the mass is poured on to a dry filter paper and the nitrogen in 20 or 40 c.c. of the filtrate determined with Knop's azotometer (*cf.* p. 125), and the quantity of nitrogen absorbed from the solution by 50 g. of soil found by difference. The amount of nitrogen absorbed by 100 g. of soil and expressed in c.c. is called the "absorption quantity," and serves as an expression for the absorptive power.

R. Gans, in determining absorptive power by Knop's method, uses fine earth which has passed through a 2 mm. sieve, partly because this is used as the material for all other investigations of soil, and also because the preparation of large quantities of fine earth under 0.5 mm. diameter is troublesome. He further regards the use of calcium carbonate as unnecessary, since no hydrochloric acid is liberated, and as inadmissible because it promotes the formation of zeolitic bodies from clay-like substances and of calcium salts of humic acid, the two classes of compounds which are mainly concerned in ammonia absorption.

**Evolution of Heat on Moistening.** — According to A. Mitscherlich,<sup>1</sup> all the results of the mechanical and physical examination of soils can be expressed in terms of one magnitude by determining the evolution of heat on moistening with water; Bunsen's ice calorimeter, as improved by Schuller and Wartha, is used for the estimation. This property is, according to Wilhelmy, dependent upon the size and shape of the surface, and also upon the specific adhesion constants of the individual earth particles.

Other physical properties, which are of importance in judging the fertility of soil, include the evaporation capacity, the filtration capacity, the absorptive capacity for water vapour, and for oxygen, the permeability to air, the relation of soil to heat, etc.<sup>2</sup>

The difficulty in connection with all these physical investigations of the soil, is not in carrying out the processes, but in interpreting the results. It is only in the most general way that any relation can be made out between the texture of the soil and the physical constants thus determined; nor are any similar data for known soils available which might be compared with the results obtained by any of the methods described above. These methods, in fact, have been suggested on theoretical grounds alone, and the figures they yield have never been correlated with the behaviour of the soil in the field.

#### IV. CHEMICAL EXAMINATION

For the chemical examination of soil a sample of fine earth is taken which has been dried in the air, but not previously ignited, and then

<sup>1</sup> *J. f. Landw.*, 1898, 46, 255; *Landw. Jahrb.*, 1901, 30, 361.

<sup>2</sup> For further details, *cf.* Wiley, *loc. cit.*, pp. 93-181.

passed through a 3 mm. sieve. The soil is then treated successively with hot, concentrated hydrochloric acid and with a 1 per cent. solution of citric acid.

**Treatment with hot, concentrated Hydrochloric Acid.**—Fifty g. of the unignited fine earth, which has passed through the 3 mm. sieve, are placed in an Erlenmeyer flask of Jena glass, covered with 100 c.c. of concentrated hydrochloric acid, the flask loosely stoppered with a bulb blown on a piece of glass tubing, and gently boiled for five to ten minutes. It is then heated on the water-bath for forty-eight hours, the contents diluted, filtered, and made up to a convenient bulk for the determination of the total potassium and phosphoric acid, and of iron, calcium, magnesium, sodium, and sulphuric acid if desired.

**Treatment with Citric Acid.**—Two hundred g. of the air-dried fine earth, which has passed through the 3 mm. sieve, are placed in a Winchester quart bottle, and 20 g. of citric acid and 2 litres of water added. The whole is well shaken and allowed to stand, with occasional shakings, for a week. The "available" phosphoric acid and potash are determined in the solution obtained.<sup>1</sup> By using a continuous end-over-end shaking machine the time of extraction may be reduced to one day. For the determination of the total potassium an aliquot portion of the solution is evaporated to dryness, ignited to get rid of organic matter, the residue taken up afresh with strong hydrochloric acid, filtered, again evaporated to dryness, and heated in an air-oven to 110° to 120° for an hour to render any silica insoluble. The residue is taken up with dilute hydrochloric acid, filtered, and evaporated on the water-bath with 25 c.c. of a solution of platinic chloride containing 5 g. of platinum per litre. When a crystalline magma has resulted from the evaporation the mass is transferred to a filter (most conveniently a small Gooch or Buchner filter), washed with alcohol until the excess of platinic chloride is removed, and then with a solution of ammonium chloride (1 : 5) which has been saturated with the double chloride of ammonium and platinum, to remove any traces of silica, calcium sulphate, etc., and finally again with alcohol. The double salt remaining on the filter is dissolved off with hot water, evaporated in a small tared basin, and weighed; it contains 19.31 per cent. of  $K_2O$ . Or, the solution may be reduced by heating with formic acid and a few drops of sulphuric acid, the platinum collected on a filter, ignited, and weighed.

For the determination of phosphoric acid an aliquot portion of the solution is similarly evaporated, ignited, taken up with hydrochloric acid, again evaporated, and heated to 120° as described above. The residue is taken up with dilute hydrochloric acid, filtered into a beaker (the bulk should not exceed 100 c.c.), and about 5 g. of ammonium

<sup>1</sup> Cf. B. Dyer, *J. Chem. Soc.*, 1894, 65, 115.

nitrate and 50 c.c. of a solution of ammonium molybdate containing 60 g. of molybdic acid per litre added. The mixture is put aside in a warm place (not exceeding  $40^{\circ}$ ) for twenty-four hours and the precipitate filtered off. The precipitate may then be treated in one of the three following ways:—

(1) Dissolve the precipitate in ammonia and precipitate as magnesium ammonium phosphate (p. 406). The quantity is usually too small to render this method desirable.

(2) Wash with ammonium nitrate solution, dissolve in ammonia into a tared porcelain dish, evaporate, and ignite gently over an Argand burner until no more fumes are evolved. The resulting residue contains 3.794 per cent. of  $P_2O_5$ .

(3) Wash with 3 per cent. solution of sodium nitrate, and dissolve the contents of the filter into a beaker by means of a measured volume of  $N/2$  or  $N/10$  standard alkali; then add phenolphthalein and titrate back to neutrality with the corresponding standard acid.<sup>1</sup> One c.c. of normal alkali = 0.003082 g.  $P_2O_5$ .

For the determination of the "available" constituents, two portions of 500 c.c., of the solution in 1 per cent. citric acid, are evaporated to dryness, ignited to get rid of organic matter, and treated as described. The accuracy of estimations of phosphoric acid and of potash in soils greatly depends on removing all traces of organic matter, and especially of silica, before precipitation.

In the method agreed to by the Union of Agricultural Experimental Stations in Germany for the chemical examination of soils, the sample is treated successively with the following reagents:—

- A. Water containing carbonic acid.
- B. Cold, concentrated hydrochloric acid.
- C. Hot, concentrated hydrochloric acid.
- D. Concentrated sulphuric acid.
- E. Hydrofluoric acid.

**A. Treatment with Water containing Carbonic Acid.**—One thousand five hundred g. of soil are well shaken up with 6000 c.c. of aqueous carbon dioxide solution, in a stoppered bottle. The carbon dioxide solution is prepared by saturating 1500 c.c. of distilled water with carbon dioxide at the ordinary temperature and pressure, and diluting with 4500 c.c. of water. The mixture of the sample and carbon dioxide solution is kept for three days, with frequent shaking, then allowed to settle, and 4000 c.c. of the liquid poured off and filtered through a double filter paper, the funnel being covered during the filtration; the filtered liquid represents two-thirds of the original quantity, *i.e.*, 1000 g. of the soil. An aliquot portion is evaporated to dryness in a platinum dish, dried at  $125^{\circ}$ , and weighed; the total amount of

<sup>1</sup> Cf. *United States Department of Agriculture, Division of Chemistry, Bulletin, 46, 1899, p. 13.*

dissolved matter is thus found. To estimate the dissolved mineral matter the residue is gently ignited, with repeated treatment with ammonium carbonate, and weighed; this residue may be used for the determination of the individual substances dissolved.

**B. Treatment with cold, concentrated Hydrochloric Acid.**—Seven hundred and fifty g. of soil are placed in a stoppered bottle with 1500 c.c. of 25 per cent. hydrochloric acid, and the mixture kept for forty-eight hours at the ordinary temperature, with frequent shaking. The hydrochloric acid must be free from arsenic, as otherwise incorrect values are obtained in the subsequent determination of phosphoric acid. If carbonates are present in the soil, hydrochloric acid of such strength must be taken, that two parts by volume of 25 per cent. hydrochloric acid remain, after decomposition, for every one part by weight of air-dry soil.

One thousand c.c. of the liquid are then decanted and evaporated to dryness on the water-bath, with addition of a few c.c. of nitric acid, to oxidise ferrous salts and organic matter. Silica is separated in the usual manner by repeatedly moistening the residue with hydrochloric acid and drying at  $100^{\circ}$  to  $105^{\circ}$ . The residue is dissolved in dilute hydrochloric acid, diluted, without filtering from the precipitated silica, to 1000 c.c., the solution filtered through a pleated filter paper, and three separate portions of the filtrate used for the determination of (1) iron, aluminium, manganese, calcium, and magnesium; (2) sulphuric acid and alkali; and (3) phosphoric acid.

The estimation of these constituents is then carried out in the ordinary way as follows:—Iron and aluminium are precipitated, together with any phosphoric acid, as basic acetates containing phosphates, by means of sodium acetate, the precipitate dissolved in sulphuric acid and the solution divided into two equal portions. In one portion the sum of the iron oxide, alumina, and phosphorus pentoxide is determined, and in the other half the iron is titrated with potassium permanganate solution after reduction. The difference between these two determinations gives the alumina and phosphorus pentoxide, from which the alumina is calculated after the separate estimation of the phosphoric acid. Manganese is conveniently separated as peroxide by the action of bromine on the filtrate from the precipitation with sodium acetate; the resulting manganese dioxide is dissolved in hydrochloric acid, the solution diluted with water, ammonium carbonate added in excess, and the precipitated manganese carbonate converted by ignition into  $Mn_2O_4$  and weighed. The filtrate from the manganese dioxide is heated to boiling to expel chlorine, neutralised with ammonia, and the calcium precipitated with ammonium oxalate, filtered after standing for some hours, ignited, and weighed as calcium oxide. The magnesium is estimated in the filtrate, containing ammonium oxalate, by adding

ammonia and sodium phosphate, filtering after standing for twelve hours, igniting the precipitate, and weighing as  $\text{Mg}_2\text{P}_2\text{O}_7$  (*cf.* p. 406).

The sulphuric acid is separated and weighed as barium sulphate after precipitation with barium chloride. The filtrate is warmed, treated with ammonia and ammonium carbonate, filtered, the precipitate washed with hot water till free from chlorides, and the filtrate and washings then evaporated to dryness on the water-bath in a large platinum or glazed porcelain dish. The dry ammonium salts are, in the latter case, transferred to a smaller platinum dish with a platinum spatula and carefully volatilised; after cooling, the residue in the porcelain dish is rinsed into the platinum dish, treated with oxalic acid, evaporated on the water-bath, and carefully ignited. The oxalates are thus converted into carbonates, and any remaining magnesium, calcium, barium, manganese, aluminium, etc., can then be separated from the alkali metals. The ignited residue is treated with hot water, filtered, the filtrate acidified with hydrochloric acid, and evaporated to dryness in a platinum dish; the residue is then gently ignited and the total alkali metals weighed as chlorides. These are then redissolved in water, filtered, the filtrate evaporated to dryness with platinum chloride treated with alcohol, the precipitate of potassium platinichloride collected on a tared filter paper, and weighed. The potassium chloride found, deducted from the weight of total alkali chlorides, gives the weight of sodium chloride.

To determine phosphoric acid, the original solution is repeatedly evaporated to dryness with nitric acid, the residue finally dissolved in nitric acid, and the liquid precipitated with ammonium molybdate. Phosphoric acid may also be quickly determined as follows, according to M. Märcker: 25 g. of soil are boiled for half an hour with 20 c.c. of fuming nitric acid and 50 c.c. of concentrated sulphuric acid. After cooling, the solution is diluted to 500 c.c., of which 100 c.c. are used for the precipitation. This portion is made alkaline with ammonia, re-acidified slightly, and treated, after cooling, with 50 c.c. of Märcker's citrate solution and 25 c.c. of magnesia mixture; it is then stirred mechanically for half an hour, and filtered after standing for from twenty-four to forty-eight hours. The citrate solution is prepared by dissolving 1100 g. of pure citric acid in 4000 g. of 24 per cent. ammonia, and diluting with water to 10 litres.

**C. Treatment with hot, concentrated Hydrochloric Acid.**—One hundred and fifty g. of soil are heated to boiling, with frequent shaking, with 300 c.c. of concentrated pure hydrochloric acid of sp. gr. 1.15, then boiled for exactly one hour, diluted with water to a definite volume, and filtered. The filtrate is examined as described under B.

**D. Treatment with concentrated Sulphuric Acid.**—The residue from C. is dried in the air, weighed, and a portion extracted with

sulphuric acid. For this purpose it is stirred up with sulphuric acid in a platinum dish to a thin paste, the sulphuric acid volatilised on a sand-bath or asbestos plate with a very small flame, and the operation repeated two or three times. The residue is evaporated to dryness with hydrochloric acid on the water-bath, heated for a short time in an air-oven, and then treated with water containing hydrochloric acid, and filtered. Aluminium, iron, calcium, magnesium, and the alkali metals are determined in the filtrate as described under B. Silicic acid, sand, and silicates remain in the residue; the silicic acid is removed by boiling with sodium carbonate solution, leaving quartz and silicates, which are weighed after drying and incinerating the filter paper; they are then finely ground in an agate mortar and part of the product used for E.

**E. Treatment with Hydrofluoric Acid.**—It is convenient to use this acid in aqueous solution. For the treatment, the above residue is moistened with water in a platinum dish and strong hydrofluoric acid then poured on to it; the dish is covered and kept for two to three days, the contents being frequently stirred with a platinum spatula, until the whole mass has broken up to a paste. The hydrofluosilicic acid which has been formed is then expelled by evaporating on the water-bath to dryness, the residue moistened with concentrated sulphuric acid and the latter volatilised by heating. The residue is then boiled with water containing hydrochloric acid; if it does not dissolve completely it is filtered and the residue again treated with hydrofluoric acid. Aluminium, calcium, magnesium, potassium, and sodium are determined in the united filtrates according to the methods described above.

In place of hydrofluoric acid it is more convenient to use ammonium fluoride, which can be obtained in a pure state. The finely ground material obtained as above, or the original soil ground in an agate mortar, is weighed into a platinum crucible and covered with solid ammonium fluoride. The mixture is well stirred with a platinum spatula, a little more ammonium fluoride added, and any material adhering to the spatula washed off with a few drops of water. The lid is then placed on the crucible and the whole gently ignited over an Argand burner, gradually raising the heat until, after an hour or two, no more fumes are observed. After cooling, the residue in the crucible is moistened with strong sulphuric acid and ignited, at first gently, and then at a low red heat. The material remaining in the crucible is then extracted with strong hydrochloric acid, in which it should be completely soluble, except in the rare cases when barium sulphate forms a constituent of the soil.

THE DETERMINATION OF THE INDIVIDUAL CONSTITUENTS  
OF SOIL

**Hygroscopic Moisture.**—Five to ten g. of the air-dried sample are heated in the air-bath to  $100^{\circ}$  to  $105^{\circ}$ , until the weight is constant.

**Chemically combined Water or Loss on Ignition.**—Apart from hygroscopic, mechanically absorbed moisture, soil contains chemically combined water in the form of hydrates, gypsum, clay, etc., which is not removed by drying at  $100^{\circ}$ . This is estimated by gently igniting 10 g. of the sample until all organic matter is destroyed, treating repeatedly with ammonium carbonate, and subsequently igniting until the weight is constant. By deducting from the total loss thus estimated the quantity of organic matter determined as described below and of hygroscopic moisture, the quantity of chemically combined water is found. The result is, however, only approximately correct, as part of the carbon dioxide is lost on ignition if large quantities of alkali earth carbonates are present and any ferrous oxide is converted into ferric oxide.

According to the decision of the Union of German Agricultural Experimental Stations, the loss on ignition is determined by drying the soil at  $140^{\circ}$ , igniting, moistening with ammonium carbonate solution, and again igniting gently. If, as is here assumed, the chemically combined water is volatilised at  $140^{\circ}$ , the loss on subsequent ignition in this case corresponds to the amount of organic matter present. This method cannot be used in the case of peat soils or of other soils which contain large quantities of humus substances, as these latter undergo considerable decomposition at  $120^{\circ}$ .

The water chemically combined with the double silicates in the clay is not expelled even at a low red heat, and it is difficult to obtain exactly concordant results for the loss on ignition, except by ignition at a high temperature over the blow-pipe. It is, on the whole, better, after determining the hygroscopic moisture, to ignite at a low temperature below visible redness over an Argand burner for some hours, with occasional stirring, until the soil is at a bright red heat; at this temperature neither the carbonates nor the clays are decomposed, and the loss of weight more nearly represents the organic matter only.

**Humus.**—G. Loges' method<sup>1</sup> for the estimation of humus substances, which has been adopted by the Union of German Agricultural Experimental Stations, is as follows:—Five to ten g. of soil are evaporated to dryness in a Hoffmeister glass dish on the water-bath with dilute phosphoric acid, which is to be preferred to sulphurous acid. This treatment serves to remove any pre-formed carbon dioxide. The dry soil, together with the glass dish, are ground up with powdered copper

<sup>1</sup> *Landw. Versuchsst.*, 1883, 28, 229; 1891, 38, 311.



oxide and placed in a combustion tube 60 cm. in length and open at both ends; the layer of mixed earth and copper oxide is separated by a little asbestos from a succeeding layer of granulated copper oxide of 20 cm. length, which is, in turn, succeeded by a spiral of copper or silver gauze, 10 to 12 cm. long, to reduce nitrogen oxides and to retain chlorine. The combustion tube is connected with a calcium chloride tube and potash bulbs, and the combustion carried out in the usual manner; the increase in weight of the potash bulbs gives the weight of carbon dioxide formed by the combustion of the humus.

If the pre-formed carbon dioxide of the soil is not first removed, it must be determined separately and deducted from the total carbon dioxide found.

Warington and Peake<sup>1</sup> have proposed the following method for determining the carbon:—Ten g. of soil, first freed from carbonates by warming gently with a concentrated sulphurous acid solution, are evaporated to dryness on the water-bath, the residue transferred to a platinum boat, and combusted in a tube, the front part of which is filled with copper oxide, in a current of oxygen.

The many methods which have been proposed of oxidising in the wet way, either with chromic acid or with sulphuric acid and potassium permanganate, all give low results, and are therefore not applicable to the analysis of soil. According to experiments of G. Loges, only from 64 to 96 per cent. of the total carbon is obtained in this way; Warington and Peake found from 72 to 83 per cent. of the total carbon present by using chromic acid, and from 89 to 95 per cent. with permanganate.

The error in Warington's and Peake's method is due to the fact that some of the carbon compounds in the soil are only partially oxidised to acetic acid, etc. By passing the gases from the chromic acid oxidation through a short length (20 cm.) of combustion tube containing heated copper oxide and then through a little silver sulphate solution before reaching the calcium chloride and potash absorption tubes, results can be obtained which agree very closely with those obtained by the ordinary combustion process.<sup>2</sup>

The content of humus, free from water and nitrogen, can be calculated from the weight of carbon dioxide found, on the basis of H. Wolff's estimate of the percentage of carbon in humus as 58. The quantity of humus is therefore obtained by multiplying the carbon dioxide found by 0.4702, or the carbon by 1.724.

The "soluble humus" is often determined as follows:—Forty g. of the soil are first warmed with a little dilute hydrochloric acid to remove carbonates and to break down humates; the soil is then transferred to

<sup>1</sup> *J. Chem. Soc.*, 1880, 37, 617.

<sup>2</sup> Cf. Hall, Miller, and Marmu, *J. Chem. Soc.*, 1906, 89, 595.

a filter, well washed, dried, brushed into a cylinder of about 250 c.c. capacity, and 200 c.c. of a solution containing one part of strong ammonia in five parts of the solution added. The whole is well shaken at intervals during the day, and left for a day or two to settle. Fifty c.c. of the supernatant dark liquid are then pipetted off, evaporated in a porcelain basin to dryness, and weighed; the residue is then ignited and the weight of the "soluble humus" obtained from the difference in the two weighings.

Some idea of the nature of the humus substances may be gathered from the following considerations:—

The ratio of carbon to nitrogen is a useful indication; the nearer this is the better if an average amount of humus (3 to 4 per cent.) is present.<sup>1</sup> The ratio of organically combined nitrogen to carbon varies from 1 : 5 to 1 : 40.

The degree of decomposition and decay of the humus is ascertained by a microscopical examination of the various products of elutriation and by their loss of weight on ignition.

The reaction of the soil is observed by laying it, whilst fairly moist, on sensitive litmus paper. A temporary reddening of the paper, which disappears on drying, is due to carbon dioxide. If a permanent acid reaction is obtained, the amount of free acid may be approximately determined by boiling 50 g. of the soil with water, and titrating the mixture with dilute barium hydroxide solution until it is slightly alkaline.

Knop<sup>2</sup> has proposed to determine the capacity of the soil for absorbing lime, which is almost entirely due to humus substances as a measure of the quantity present. For this purpose 100 g. of soil are kept in contact with 200 c.c. of an ammoniacal calcium nitrate solution for twenty-four hours, with shaking, the solution filtered, and the lime determined in a portion of the filtrate. The ammoniacal calcium nitrate solution contains 1 g. CaO per 200 c.c. and an equivalent amount of ammonia. Hall regards this determination as quite valueless.

**Carbon Dioxide.**—The combined carbon dioxide may be determined either by loss or by absorption, by the usual methods.

According to Immendorff<sup>3</sup> the results obtained in the case of humus soils containing small amounts of alkali earth carbonates, are inaccurate because the humus substances form appreciable quantities of carbon dioxide, when heated with water or with dilute acids in presence of oxygen, or even in an atmosphere of hydrogen. He therefore recommends that heating should be dispensed with and the reaction carried out at the ordinary temperature; the dolomitic material in soil is so finely divided that it is completely decomposed by continuing the action of cold hydrochloric acid for about three hours.

<sup>1</sup> Cf. Lawes and Gilbert, *J. Chem. Soc.*, 1885, 47, 380; also, A. D. Hall, *The Soil*, p. 44.

<sup>2</sup> *Landw. Versuchsst.*, 8, 40.

<sup>3</sup> *Z. angew. Chem.*, 1900, 13, 1177.

When the soil contains only small proportions of calcium carbonate, less than 1 per cent., it is almost impossible to obtain accurate results by the ordinary gravimetric methods. A method depending upon the measurement of the volume of carbon dioxide evolved on treatment of the soil with sulphuric acid at low pressures, and which can be used in such cases, has been devised by Hall and Russell.<sup>1</sup> The most accurate results for small quantities are obtained as follows: Fifty g. of the soil are placed in a small flask furnished with a stoppered funnel and an inlet and exit tube. Air freed from carbon dioxide is drawn by means of a pump, through the flask and into a small Reiset tower containing a known volume of normal sodium hydroxide solution, made free from sodium so as to be free from iron, alumina, silica, etc. The soil is decomposed by hydrochloric acid, delivered through the stoppered funnel and the evolved carbon dioxide expelled by bringing the contents of the flask to a gentle boil while the air current is passing; the current is continued until all the evolved gas has been swept forward. The carbon dioxide is absorbed in the Reiset tower and is determined by a double titration. Phenolphthalein is first added, and normal hydrochloric acid run in little by little, with shaking, until the pink colour is ready to disappear. The final disappearance of the pink colour is carefully brought about by the use of  $N/10$  hydrochloric acid solution; the volume of acid used up to this stage need not be recorded, as this forms only the starting-point for the titration proper, when the carbon dioxide is all combined as bicarbonate. Methyl orange is then added, and the titration continued with an accurately prepared  $N/10$  hydrochloric acid solution until a change of colour takes place. The hydrochloric acid used in this latter estimation is alone taken into account, and is equivalent to the carbon dioxide set free from the state of bicarbonate. A blank titration must also be made of the sodium hydroxide solution used for the absorption, and a correction made for any carbon dioxide contained.<sup>2</sup>

The carbon dioxide contained in the air occluded in the soil is an indication of the amount of organic matter present and of the extent of the processes of decomposition that have occurred. Its determination hardly falls within the scope of the ordinary analysis of soils, but may be necessary in the case of special investigations. To carry out the estimation a fairly large cylindrical hole is made in the soil, several gas- or lead-pipes placed in it, to the required depth, and the hole either allowed to fall together or filled in with the displaced soil. After a few days the ends of the tubes, which are allowed to project about 15 cm. above the surface of the soil, are connected with a wash-bottle containing concentrated sulphuric acid, and then with a Pottenkofer's

<sup>1</sup> *J. Chem. Soc.*, 1902, 81, 18.

<sup>2</sup> Cf. Brown and Escombe, *Phil. Trans. B.*, 1900, 193, 223.

absorption tube containing a measured volume of barium hydroxide solution of known strength. The air is then aspirated through the apparatus, and after the absorption is completed the excess of barium hydroxide titrated back with oxalic acid, using rosolic acid as indicator. If the gravimetric determination of carbon dioxide is preferred, weighed potash bulbs, connected at each end with calcium chloride tubes, are used.

Before starting the determination, about 1 litre of the air should first be aspirated through the pipes, and the absorption apparatus then attached.

**Total Nitrogen.**—This is determined by Kjeldahl's method, unless nitric acid is present, when Jodlbaur's method (p. 817) must be used; the quantity of nitrates in cultivated soils is, however, so small that there is no necessity to adopt the latter modification. In either case, 1 to 2 g. of peaty or moorland soil, 2 to 5 g. of peaty sand soil, or 5 to 10 g. of ordinary arable soil, are used for the estimation; the sample must be air-dry and finely divided. To prevent bumping during distillation the liquid is diluted after the decomposition with a little water, poured off from residual sand, the latter shaken up repeatedly with small quantities of water, and the ammonia distilled off from the united liquid and washings in the usual manner.

**Ammoniacal Nitrogen.**—Only very small quantities of ammonia are usually present in soil. It is determined, according to E. Wolff, as follows:—One hundred g. of fine earth are mixed with 500 c.c. of water into which 5 g. of freshly ignited magnesia have previously been stirred, and 200 c.c. distilled off at a moderate boil, preferably on a sand-bath, as the mixture does not boil satisfactorily over a naked flame; the ammonia given off is absorbed by sulphuric acid of known strength.

The following method may also be employed:—One hundred g. of fine earth are placed in a weighed flask of 1 to 2 litres capacity, and 50 c.c. of dilute hydrochloric acid added. After all the carbon dioxide has been liberated, more dilute acid is added until, after shaking repeatedly, it is in decided excess. The liquid is then diluted to about 400 c.c. with water free from ammonia, mixed thoroughly, and the whole weighed. The soil is then allowed to settle, the clear, supernatant liquid carefully syphoned off, and the contained ammonia estimated by distillation with ignited magnesia. The weight of liquid removed is determined by again weighing the flask and contents; to determine what proportion of the total extract has been taken, the undissolved residue is filtered off, washed, dried at 125°, weighed, and its weight deducted from that of the total contents of the flask.

**Nitric - Nitrogen.**—In preparing soil for a determination of nitrates, it is necessary that the sample be dried quickly, by spreading it out in thin layers, as soon as it comes from the field, and keeping it in an oven at a temperature of about 60°. During air-drying a notable increase takes place in the amount of nitrates present.

The determination is best carried out as follows:—From 300 to 500 g. of the air-dried soil are packed on a large Buchner funnel, connected with a water-pump, and distilled water added until the soil is saturated. The pump is then started and successive small additions of water are made until about 100 c.c. have drained through. This extract contains the whole of the nitrates and chlorides in the soil. The nitrates are conveniently determined by reduction with a zinc-copper couple, in a warm place for forty-eight hours, followed by distillation with magnesia and estimation of the ammonia by Nessler's reagent.<sup>1</sup>

As an alternative method, 1000 g. of air-dried fine earth are mixed with so much water that the total quantity of water, including the moisture present in the soil, is 2000 c.c. The mixture is allowed to stand for forty-eight hours, with frequent shaking. The clear liquid is then poured through a filter, and 1000 c.c. of the filtrate evaporated down to a small volume, with addition of a little sodium carbonate. If considerable quantities of soluble humus substances are present, they are precipitated by boiling the liquid with milk of lime, and the excess of lime separated, after filtration, by a current of carbon dioxide; the liquid is then filtered, and the nitric acid determined in the filtrate by the methods of either K. Ulsch, Schlösing, or Böttcher, etc. (*cf.* pp. 309 and 822).

**Organic Nitrogen.**—This is calculated by subtracting the ammoniacal nitrogen and the nitric-nitrogen from the total nitrogen found.

**Chlorine.**—The chlorides are washed out of the soil by the treatment described under "nitric-nitrogen," and are estimated by titration with *N*/100 silver nitrate solution, using potassium chromate as indicator.

As an alternative method, 300 g. of air-dried fine earth are mixed with so much water that 900 c.c. are present altogether, inclusive of the moisture originally contained in the soil. The mixture is allowed to stand for forty-eight hours, with shaking, 450 c.c. of the liquid filtered off, evaporated down to about 200 c.c. with addition of a little sodium carbonate, again filtered, and the chlorine estimated, either volumetrically or gravimetrically, in the filtrate.

**Sulphur.**—Sulphur is fairly often present in soil, either in the form of metallic sulphides or of organic compounds. The determination of sulphur, in other forms than as sulphates, is often of importance, as many sulphur compounds, such as calcium sulphide, are directly injurious to plants, and others, which are harmless in themselves, such as iron sulphide, are converted by oxidation into soluble, harmful substances, such as ferrous sulphate. Moreover, the presence of such compounds indicates unfavourable physical conditions of the soil.

To determine sulphur, 25 g. of air-dried fine earth are treated in a

<sup>1</sup> *Cf.* Warrington, *J. Chem. Soc.*, 1882, 41, 351.

platinum dish with a concentrated solution of potassium nitrate and potassium hydroxide, and ignited. After cooling, the mass is extracted by boiling with dilute hydrochloric acid, with addition of a little nitric acid, evaporated to dryness to separate silica, the residue extracted with dilute hydrochloric acid, and the resulting solution precipitated with barium chloride. By deducting, from the amount of sulphuric acid found in this way, the amount found in the hot hydrochloric acid extract of the original soil, the amount of sulphur present in other forms than as sulphates is obtained.

M. Fleischer gives the following method for the estimation of sulphur, other than that present as soluble sulphates:—Twenty g. of fine earth, which has been extracted with water and dried, is ignited in a current of air in a combustion tube, by which means any sulphur compounds are decomposed, and the contained sulphur converted into sulphuric and sulphurous acids. The substance is placed loosely in the combustion tube, between two plugs of glass-wool; one end of the tube is connected with a wash-bottle containing water, to control the amount of aspirated air, whilst the other end is bent over, drawn out a little, and connected with a Peligot U-tube containing potassium hydroxide solution, free from sulphates. The Peligot tube is attached to a tube containing glass beads, moistened with potassium hydroxide solution, and this again to a glass tube, bent at right angles and provided with a bulb on the horizontal arm. Neutral litmus solution is placed in the bulb; it should not change colour during the estimation. An aspirator is attached to the end of the apparatus. The combustion tube is heated till red-hot, starting from the back and proceeding to the front, air being meanwhile aspirated continuously through the apparatus. The products of distillation, which condense in the front end of the combustion tube, must be driven into the absorption apparatus by careful heating. The potassium hydroxide solution is then treated with an excess of nitric acid and with bromine to oxidise any sulphurous acid, the excess of bromine expelled by boiling, and the sulphuric acid precipitated, as usual, with barium chloride.

In the case of peat, or moorland soils, the combustion is best carried out in a current of oxygen.

According to the method proposed by F. Wahnschaffe, 5 to 10 g. of the soil, previously extracted with water, are heated in a sealed tube with 20 c.c. of water and 5 c.c. of bromine. The tube is gradually heated up to 70° in a water-bath, with frequent shaking, and finally to 75°. The contents are poured into a beaker, diluted with water, boiled until the excess of bromine is removed, filtered, and the sulphuric acid precipitated in the filtrate with barium chloride. The method is inapplicable if large quantities of gypsum are present, as in this case the sulphates are not completely extracted by water.

**Ferrous Iron.**—The injurious effect of ferrous salts, especially if present in a soluble form, is well known; the lack of fertility of a soil is often solely due to their presence. Unfortunately, the presence of organic matter often renders their exact determination impossible. Their qualitative detection is, however, often sufficient, especially if their solubility is taken into account. For this purpose the soil is treated, in an atmosphere of carbon dioxide, with various solvents, such as water, dilute acetic acid, hot and cold hydrochloric acid, sulphuric acid, solutions of neutral tartrates, etc., and the solutions obtained tested qualitatively with potassium ferricyanide.

To determine ferrous iron quantitatively, 10 g. of the air-dried soil are placed in a 250 or 500 c.c. graduated flask, the air of the flask displaced by a current of carbon dioxide, 100 c.c. of dilute sulphuric acid (1 : 3) added, and the flask closed by means of a Bunsen valve. The mixture is then digested on the water-bath for about two hours, with frequent shaking, allowed to cool, and filled up to the mark with boiled distilled water to which dilute sulphuric acid has been added, so that the mixture is very strongly acid. The contents are then well mixed, the closed flask allowed to stand until the sediment has settled completely, and an aliquot part of the clear liquid removed, and titrated with  $N/10$  potassium permanganate solution, the first redness which persists for some seconds, being taken as indicating the end of the reaction. The results obtained by this method are apt to be too high in the case of soils containing much humus, as the dissolved organic matter acts on cold permanganate solution.

**Copper and Lead.**—These metals are sometimes present in natural soils, and may also be introduced by refuse from works, or by manuring with street sweepings or with domestic refuse. They are determined by passing hydrogen sulphide into a warm hydrochloric acid extract of the soil; if the presence of zinc is suspected, a greater excess of hydrochloric acid must be added, as otherwise zinc is also partially precipitated. According to the experiments of R. Grundmann, 30 c.c. of hydrochloric acid of sp. gr. 1.1 are added to about 250 c.c. of the solution, and hydrogen sulphide passed in at about 70° until present in large excess; the liquid is filtered before the excess of hydrogen sulphide has had time to escape or be decomposed, the precipitate washed with water containing hydrogen sulphide, dried, ignited, dissolved in aqua regia, the solution evaporated to dryness, treated with water and hydrochloric acid, and again precipitated with hydrogen sulphide. The precipitate thus obtained, which is free from zinc, is again filtered, washed, dissolved in nitric acid, the solution diluted with distilled water, and filtered. The filtrate is treated with pure sulphuric acid in fair excess, evaporated till the sulphuric acid begins to volatilise, allowed to cool, treated with water, one-third of the total volume of alcohol

added, and the lead sulphate filtered off. Should the residue not contain sufficient free sulphuric acid, dilute sulphuric acid must be added previously to diluting with water. The precipitate is washed successively with water containing sulphuric acid and with alcohol, dried, ignited in a porcelain crucible, and weighed as lead sulphate.

Copper is determined in the filtrate from the lead sulphate by boiling the liquid and adding potassium hydroxide solution; the precipitated copper hydroxide is filtered off, washed with hot water, dried, ignited in a porcelain crucible, and weighed as copper oxide.

**Zinc.**—The two filtrates from the hydrogen sulphide precipitates are united, the excess of hydrogen sulphide removed by boiling, and the zinc determined as follows:—Iron is first precipitated by sodium acetate, the solution filtered, and the zinc precipitated from the filtrate by hydrogen sulphide in warm solution. After standing for twelve hours in a warm place, the zinc sulphide is filtered off and washed with water containing hydrogen sulphide. To remove any possible traces of iron from the precipitate, it is dissolved in dilute hydrochloric acid, the solution boiled with a little potassium chlorate, and ammonia added in excess to precipitate the iron. The ferric hydroxide is removed by filtration, the filtrate acidified with acetic acid, hydrogen sulphide passed into the warm solution, and the whole allowed to stand for twelve hours. The zinc sulphide is then filtered off, washed as described above, again dissolved in hydrochloric acid, oxidised as described, and precipitated from the boiling hydrochloric acid solution as zinc carbonate by sodium carbonate, after previously nearly neutralising the solution with sodium hydroxide. The liquid is then boiled until all free carbon dioxide is expelled, as this holds zinc carbonate in solution, filtered at once, washed with hot water, dried, ignited in a platinum crucible, and weighed as zinc oxide.

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## AIR<sup>1</sup>

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English translation revised by CHARLES A. KEANE, M.Sc., Ph.D.

OXYGEN, nitrogen, argon, and carbon dioxide are the chief constituents of fresh air, and the proportions in which they occur are remarkably constant. In addition, varying quantities of moisture, and traces of hydrogen peroxide, ozone, ammonia, and nitrous acid are also present, as well as minute proportions of hydrogen and of the recently discovered monatomic gases, helium, neon, krypton, and xenon.

The air of towns is always polluted to a varying degree as the result of the combustion of fuel, respiration, and the decay of animal and vegetable matter. The proportions of the normal constituents is accordingly less constant, the traces of ozone and hydrogen peroxide present in country air are absent, and typical gaseous and solid impurities occur. The gaseous impurities include a slight excess of carbon dioxide over that found in fresh air, sulphurous acid, hydrochloric acid, certain ill-defined organic compounds, and, in exceptional cases, hydrogen sulphide and other acid gases. The solid impurities consist of carbon and carbonaceous matter, smoke, and soot, the products of the incomplete combustion of fuel in houses and in factories; dust or debris formed from the attrition of both inorganic and organic material; ammonium salts, the result of the decomposition of organic matter and living organic matter, germs or microbes. Liquid impurities are very rarely present, except in foggy weather; the globules of water of which fog consists then collect the soluble impurities in an exceptionally concentrated form.

The air of confined spaces such as dwellings, workshops, and factories, is chiefly characterised by an excess of carbon dioxide above that found in normal air, the result of respiration and of combustion; the determination of this excess is of great hygienic importance. In mines, underground railways and similar spaces, which usually necessitate some system of artificial ventilation, the air generally

<sup>1</sup> Portions of the section on "Air," contributed by Prof. Erismann to the previous German edition, have been incorporated in this section.

contains an excess of carbon dioxide above that of the surrounding atmosphere and a deficiency of oxygen; sulphur dioxide, carbon monoxide, hydrogen sulphide, and methane are characteristic impurities.

Apart from the pollution of the air in confined spaces by respiration and combustion, a considerable variety of gases and vapours may give rise to pollution, as the result of industrial processes carried out in workshops and factories, the estimation of which is of the utmost importance as a means of regulating the hygienic conditions of specific industries.

The analytical methods described in this section are accordingly grouped under the following headings:—

- I. *The estimation of the normal constituents of air.*
- II. *The estimation of the impurities that may be present in the air of towns and in that of confined spaces.*
- III. *The estimation in air, of the impurities associated with specific industries.*

A summary of the effects of the various impurities that may be present in air is given at the end of the section, and an appendix is included, containing a description of Pontag's investigations on *Tobacco Smoke*.

## I.—THE ESTIMATION OF THE NORMAL CONSTITUENTS OF AIR

### 1. Oxygen.

Oxygen is determined by absorption with either alkaline pyrogallol, phosphorus, or sodium hydrosulphite, the carbon dioxide having been previously absorbed by sodium hydroxide. Full details of the methods employed and of the apparatus used are given in the section on "Technical Gas Analysis," p. 189 *et seq.*

Apart from the ordinary methods of gas analysis, Chlopin<sup>1</sup> has devised a titration method for the estimation of the oxygen in air, based on L. W. Winkler's method for the determination of dissolved oxygen in water. The reactions on which the method depends are described in the section on "Drinking Water and Water Supplies," p. 782.

The determination is carried out in the apparatus shown in Fig. 196.

The bottle *a*, the capacity of which has been determined, together with the tube *bdg*, is placed in a vessel of water, 15 c.c. of a solution of manganous chloride introduced (40 g.  $\text{MnCl}_2 \cdot 4\text{H}_2\text{O} + 60$  c.c. water), the taps opened, and the sample of air blown through the apparatus with a bellows. The temperature of the air is assumed to be the same as that of the water; for very accurate work a thermometer is fitted to the apparatus by means of a ground stopper. The burette *c* is then

<sup>1</sup> *Arch. f. Hygiene*, 1900, 37, 323.

attached to the upper end of the tube *d*, and filled with a solution of potassium iodide and sodium hydroxide (30 g. KI + 32 g. NaOH in 100 c.c. of water), 15 c.c. of which are allowed to flow into the bottle, without taking it out of the water in which it is immersed. The apparatus is shaken until the absorption is complete, which is recognised by the transition of the original blackish-brown colour of the contents to a yellowish-brown. Finally, concentrated hydrochloric acid is poured into the bottle through the tube *d*; this dissolves the precipitate and

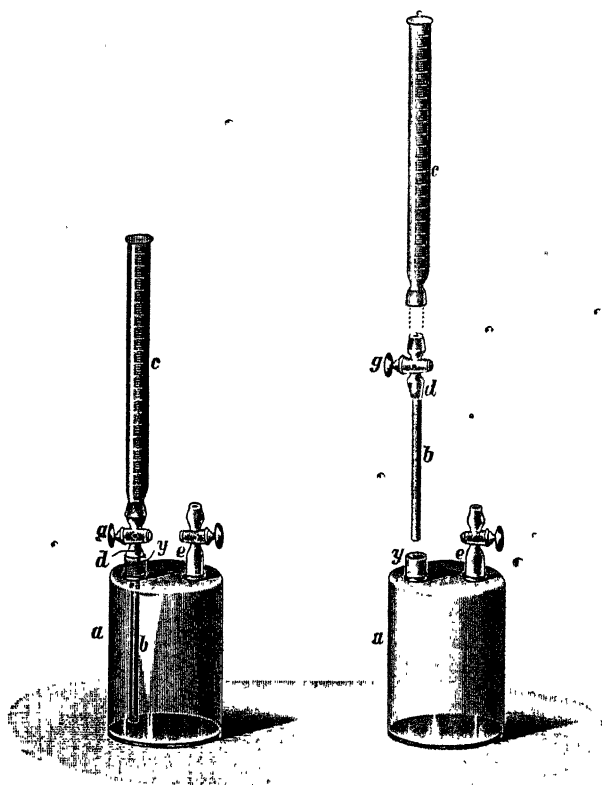


FIG. 190.

liberates iodine, which is titrated with *N*/10 sodium thiosulphate solution (24.8 g. per litre). Since the vapour tension of the manganous chloride solution at any temperature is obtained by multiplying the vapour tension of pure water by 0.857, the volume of the gas mixture at 0° and 760 mm. is found by the following formula:—

$$V^{\circ} = \frac{(V^t - 30)(B - h \cdot 0.857)}{(1 + \alpha^t)760}$$

In this equation:—

$V^{\circ}$  = the volume of the dry gas mixture at 0° and 760 mm. pressure (to be determined).

$V^t$  = the volume of the gas mixture at the temperature  $t$  and barometric pressure B.

$30$  = the volume of the reagents introduced into the apparatus.

$h$  = the tension of aqueous vapour at the temperature  $t$ .

The percentage of oxygen in the mixture of gases under investigation is calculated from the equation:—

$$x = \frac{0.5599 \cdot n \cdot 100}{V^0}$$

Where  $0.5599$  = the volume of oxygen in c.c. at  $0^\circ$  and  $760$  mm. pressure, which corresponds to  $1$  c.c. of the  $N/10$  solution of sodium thiosulphate, and  $n$  = the number of c.c. of sodium thiosulphate solution used in the titration of the iodine liberated.

The results obtained by Chlopin by this method agree closely with parallel determinations made by Bunsen's eudiometric method. He found, as the mean of a series of experiments with the apparatus without a thermometer,  $20.99$  per cent. of oxygen, and in the apparatus with a thermometer,  $20.91$ , whilst Bunsen's method gave  $20.88$  per cent. The individual analyses did not deviate more than about  $0.2$  per cent. from the results obtained by Bunsen's method, so that the error is negligible for most practical purposes.

## 2. Nitrogen.

Nitrogen is always determined by difference in the analysis of air, as in other branches of gas analysis, as no convenient method for its estimation is at present known. It is usually left as a residue after the removal, by absorption or combustion, of the other constituents; this residue includes argon, the average proportion of which in fresh air is  $0.94$  per cent. by volume, and the minute traces of the other rare gases and of hydrogen present in air.

## 3. Carbon Dioxide.

The proportion of carbon dioxide in fresh air varies with the time of day, the season of the year, and atmospheric conditions. In summer, the percentage varies from about  $0.025$  by day to  $0.035$  by night; during the winter it increases to from  $0.030$  to  $0.032$  during the day. The average for good country air may be taken as  $0.0285$  per cent.<sup>1</sup> The air of towns contains from about  $0.04$  to  $0.05$  per cent. of carbon dioxide, which increases in foggy weather to  $1$  or even more parts per thousand; Russell<sup>2</sup> found  $0.14$  per cent. in London air during a dense fog.

In dwelling-houses and other confined spaces the content of carbon dioxide may rise to several parts per thousand.

<sup>1</sup> Cf. Haldane, *Journal of Hygiene*, 1902, 2, 421; Horace Brown and Escombe, *Proc. Roy. Soc.*, 1905, 76, 118.

<sup>2</sup> *Nature*, 1891, 45, 11; *St Bartholomew's Hospital Reports*, vol. xx.

Carbon dioxide is almost always estimated volumetrically, after absorption with alkali. The method most widely used is that originally devised by Pettenkofer, in which the gas is absorbed by baryta water and the excess of the latter subsequently titrated back with oxalic acid; several modifications of this process have since been introduced. More recently a number of gas-volumetric methods have been proposed, in which the carbon dioxide is determined directly from the decrease in volume after absorption with alkali, some of which possess distinct advantages, especially when it is necessary to make a series of determinations *in situ*.

**Pettenkofer's Method.**—The following solutions are required for the determination :—

1. *Oxalic Acid.*—2.8647 g. of pure crystallised oxalic acid are dissolved in 1000 c.c. of water; 1 c.c. of this solution is = 1 mg.  $\text{CO}_2$ . Or

1.4156 g. of oxalic acid are dissolved in 1000 c.c. of water; in this case 1 c.c. is = 0.25 c.c.  $\text{CO}_2$  at  $0^\circ$  and 760 mm. The latter solution is the more generally employed. If the content of carbon dioxide is considerably above the normal, a correspondingly stronger solution of oxalic acid should be used.

2. *Barium hydroxide solution.*—

About 4.5 g. of pure crystallised barium hydroxide,  $(\text{Ba}(\text{OH})_2 + 8\text{H}_2\text{O})$  are dissolved in a litre of water, and about 0.25 g. of barium chloride added, in order to remove any alkali hydroxide which might be present.

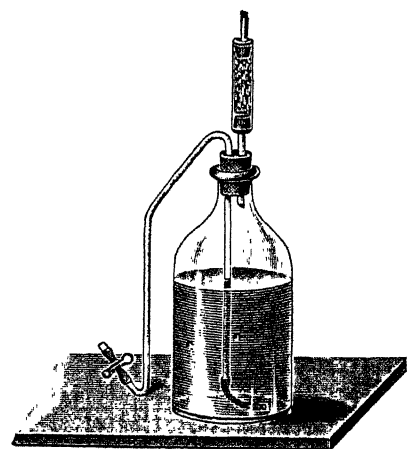


FIG. 197.

The slightly turbid liquid thus obtained is allowed to settle in a bottle, provided with a guard tube containing soda lime, and with a syphon tube as shown in Fig. 197.

The titre of the baryta water is determined by transferring 25 c.c. of the clear liquid to a small flask, and titrating with the oxalic acid solution, after adding two drops of a 1 per cent. alcoholic solution of rosolic acid or of phenolphthalein as indicator; the 25 c.c. should require about 24 c.c. of the oxalic acid solution.

The determination is carried out either in a large bottle or in a suitable absorption tube. The former method is used for estimating the amount of carbon dioxide in air at any one time, whilst the latter is preferable if the mean content of the gas in a given space is to be determined.

The bottles employed have a capacity of from 2 to 5 litres; 4 litres

is a useful average size. They are provided either with a rubber stopper or, preferably, with a cork soaked in paraffin; it is advantageous to fit the stopper with two short glass tubes, terminating flush with the bottom of the cork or stopper, each of which is capped by a small piece of glass rod attached by rubber tubing. The capacity of the flask up to the bottom of the stopper, the position of which should be marked on the flask, is calibrated with water. To collect the sample, the stopper is removed and the air to be examined introduced by a suitable bellows or aspirator, care being taken to thoroughly displace the air originally contained in the bottle (*cf.* pp. 191-2), and not to contaminate the sample by breathing into the bottle. The temperature and pressure at which the sample is collected are noted. One hundred c.c. of the barium hydroxide solution are then introduced into the bottle, by means of a pipette, either through one of the glass tubes or by slightly lifting the rubber stopper; in the latter case the glass rod attached to the second tube is slightly withdrawn to allow the displaced air to escape. The pipette is then withdrawn, and the bottle again carefully closed. The introduction of the solution may be safely carried out a quarter of an hour after sampling and in a different room if desired, provided that it is at approximately the same temperature as the place of sampling. The bottle is then gently rocked backwards and forwards, care being taken that none of the solution splashes on to the stopper; the absorption is complete in about half an hour. If several samples are under examination at the same time, it is convenient to shake each in turn for from two to three minutes at a time, so that each bottle gets from six to ten minutes' shaking during the half-hour. After the absorption the turbid liquid is quickly poured, at an open window, through a small funnel, into a stoppered bottle of a little over 100 c.c. capacity, which is then closed and allowed to stand for from one to two hours, to allow the barium carbonate to subside. Twenty-five c.c. of the clear liquid are then withdrawn, without disturbing the precipitate, and titrated as above with oxalic acid; it is advisable to titrate a second portion as a check.

In calculating the result, the capacity of the bottle is corrected for temperature and pressure, after deducting the volume of air displaced by the 100 c.c. of barium hydroxide solution introduced.

The absorption tube used in estimating carbon dioxide by this method is shown in Fig. 198.

For the determination, it is supported in a slanting position and filled to about three-quarters of its capacity (150-200 c.c.) with the barium hydroxide solution. The air is drawn through by means of the aspirator A at such a speed that the bubbles pass through singly, and from 1 to 4 litres are passed through, according to the content of the air in carbon dioxide; it is advisable to attach a second tube as a check on the absorption. When the absorption is completed, the aspirator is

detached and the contents of the tubes transferred to a suitable flask. The solution is then titrated as described above.

This form of the method is especially suitable for examining the air in difficultly accessible places, as the sample can be taken by attaching a supply tube to the absorption tube; it is also useful for estimating the total carbon dioxide evolved during a certain interval of time by a combustion or fermentation process.

The accuracy of the Pettenkofer method for the estimation of carbon dioxide in air has been very carefully investigated by Letts and Blake.<sup>1</sup> Their results show that the chief source of error is due to the action of the barium hydroxide solution on the glass of the vessel in which the sample is collected. This effect is obviated by coating the inside of the bottle with a thin layer of paraffin wax; they

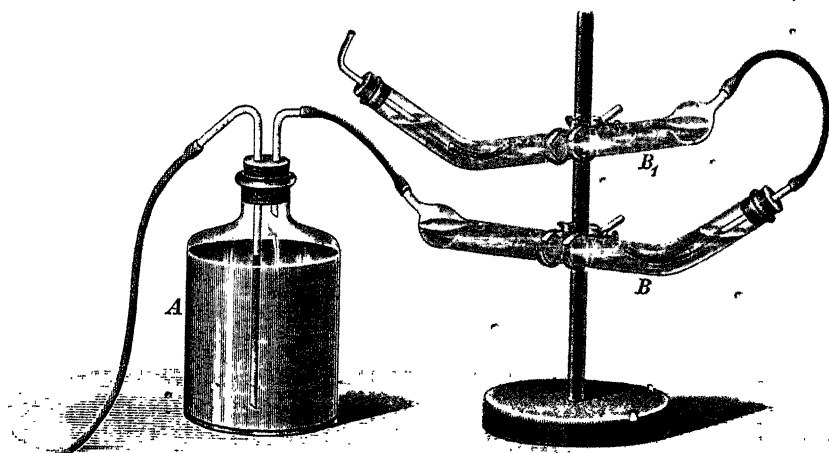


FIG. 198.

also recommend coating the inside of the bottle containing the standard barium hydroxide solution similarly. The coating is easily made by pouring melted paraffin wax into the previously warmed bottle, and then allowing the excess of wax to drain out; the capacity of the bottle must, of course, be determined after the coating of wax has been introduced. By adopting this precaution and carrying out the titrations in a vacuum, the method is rendered extremely accurate; with careful work the mean error should not exceed 0.04 parts of carbon dioxide per 10,000 by volume. Letts and Blake recommend  $N/10$  hydrochloric acid in place of oxalic acid for the determination.

Symons and Stephens<sup>2</sup> use a mixture of potassium and sodium hydroxides, containing some barium chloride, for the absorption of the carbon dioxide and acetic acid as the standard acid.

<sup>1</sup> *Chem. Soc. Proc.*, 1896, p. 192; *Proceedings of the Dublin Royal Society*, 1899 and 1900.

<sup>2</sup> *J. Chem. Soc.*, 1896, 69, 869.

The use of an absorption tube instead of a bottle in the Pettenkofer method has been developed by Reiset, Spring, and especially by Horace Brown and Escombe<sup>1</sup> in connection with their investigations on the intake of carbon dioxide into a leaf or plant, from the air. The absorbing apparatus consists of a glass tube 50 cm. long, which is fixed vertically in a wide-mouthed glass vessel furnished with a second aperture and tubulure. The bottom of the tube is closed with a platinum or silver plate, pierced with a large number of very small holes, and two other similar plates are fixed at intervals in the tube. Sodium hydroxide is used in preference to barium hydroxide as the absorbing liquid; it is placed in the lower glass vessel, and by attaching a pump to the upper part of the tube, and the air supply to be examined to the second tubulure of the glass vessel, the liquid is first drawn up into the vertical tube, and the air then follows through the perforated plates, which act as "scrubbers." The apparatus proved most efficient, and from 100 to 150 litres of air can be passed through per hour with perfect safety in regard to the complete removal of the contained carbon dioxide. With proper precautions the accuracy of the method is within 0.02 parts of carbon dioxide per 10,000 of air.

**Gas-volumetric estimation of Carbon dioxide.**—The gas-volumetric method for the estimation of carbon dioxide devised by Pettersson,<sup>2</sup> and subsequently modified by Pettersson and Palmquist,<sup>3</sup> gives very accurate results, but it is somewhat complex and accordingly unsuited for the technical examination of air.

A far simpler and very efficient apparatus has more recently been devised by Haldane.<sup>4</sup> Other simplified absorptiometric methods have been described by Gerda-Troili and Pettersson,<sup>5</sup> Teich,<sup>6</sup> and von Bleier.<sup>7</sup>

• Haldane's apparatus is shown in Fig. 199.

It consists of a measuring burette A, connected by a three-way tap B, to the absorption pipette C, and attached at the bottom to the pressure bulb D, which is suspended from the hook of the rack and pinion E. The absorption pipette is connected by a T-piece to the levelling bulb F, and to the tube G, which is provided with a three-way tap H, at the top; the tap communicates through the connections shown with the control tube J. A and J are enclosed in a rectangular water-jacket which is provided with a glass tube, through which air is blown for thoroughly mixing the contents. The measuring burette A has a capacity of about 20 c.c.; the wide upper portion is ungraduated. The

<sup>1</sup> *Proc. Roy. Soc.*, 1905, 76, 118.

<sup>2</sup> *Z. anal. Chem.*, 1886, 25, 467.

<sup>3</sup> *Ber.*, 1887, 20, 2129.

<sup>4</sup> *Ventilation of Factories and Workshops*. First Report of Departmental Committee. Blue Book [Cd. 1302], 1903, Appendix.

<sup>5</sup> *Z. für Hygiene*, 1897, 26, 57.

<sup>6</sup> *Arch. f. Hygiene*, 1893, 19, 38.

<sup>7</sup> *Z. für Hygiene*, 1898, 27, 111.



narrow lower portion, which is about 10 cm. in length, is divided into about 100 divisions, each of which corresponds to  $\frac{1}{10,000}$  part of the capacity of the burette; the lowest division is marked 0, and the readings thus give parts per 10,000 directly. The tube of the absorption pipette C and the tube G are provided with levelling marks for adjusting the pressure. The whole apparatus is fitted in a portable case, the internal dimensions of which are  $6\frac{1}{2} \times 12 \times 2\frac{1}{2}$  inches, and weighs about 5 pounds when charged ready for use.

The pressure bulb D is filled with mercury, which is used as the

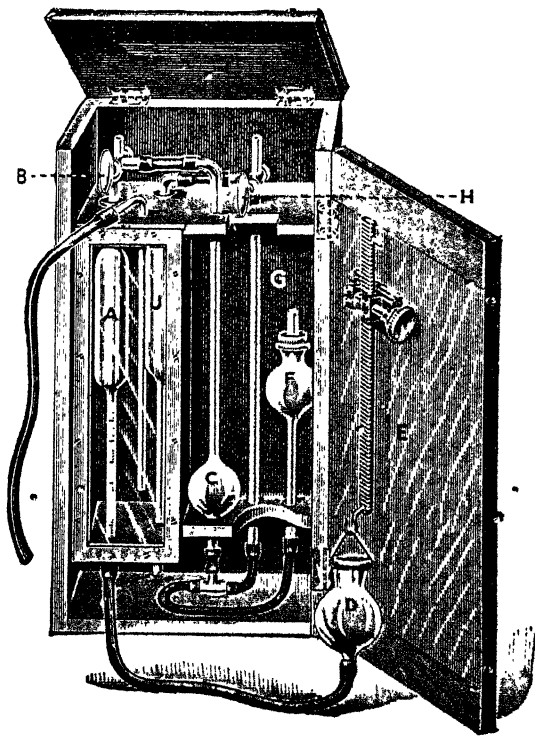


FIG. 199.

confining liquid; the absorption pipette is charged with a 10 per cent. solution of potassium or sodium hydroxide. In order to have a sharp index of the pressure under which the air is measured, the level of the solution in the narrow bore tube of the absorption pipette is taken as the index of pressure, instead of that of the mercury; the volume is adjusted to the level of the mark on this tube before and after the absorption of the carbon dioxide by raising or lowering D. The volume of air in the control tube J is adjusted before each determination by first putting it into communication with the outside air by momentarily opening the tap H, then connecting it with G, and

adjusting the level of the solution to the mark by means of the bulb F which slides easily through a loosely-fitting cork or clip. A similar adjustment is made after the absorption, so that any change of volume due to an alteration in temperature or pressure is compensated. The water in the water-jacket must be thoroughly mixed before each adjustment. To obviate error due to variations in the moisture in the air, sufficient water is introduced into both the burette and the control tube to leave a little visible moisture inside each.

To make a determination, the air in the burette A is expelled by raising D and the sample of air for analysis drawn in, to near the zero mark of the burette, by lowering D; B is then opened so as to put A into communication with C, the control tube adjusted as described, and the reading taken, after adjusting to the mark on the tube of C by raising or lowering D. The air is then driven over into C by raising the pressure bulb, and passed backwards and forwards two or three times; after finally passing back the air into the burette, the volume is adjusted as before and the reading taken. The whole estimation occupies about four minutes. The results may be relied upon to within 0.5 volumes per 10,000, after some experience with the apparatus.

**Approximate methods for the estimation of Carbon dioxide.**—For the approximate determination of carbon dioxide in air, in cases where an accuracy of 10 per cent. is sufficient, a *minimetric* method may be employed, *i.e.*, the quantity of air may be determined which is necessary to saturate the reagent used for the absorption of the carbon dioxide.

The most convenient method of this character is that devised by Lunge and Zeckendorf.<sup>1</sup> An *N*/10 solution of sodium carbonate is prepared by dissolving 5.3 g. of the anhydrous carbonate or 14.3 g. of sodium carbonate crystals in 1 litre of water, and adding 0.1 g. of phenolphthalein to the solution; the solution keeps unaltered for months, if preserved in well-stoppered bottles. Two c.c. of the solution are added to 100 c.c. of recently boiled water and allowed to cool in a closed flask. The determination is carried out in the small bottle A (Fig. 200), of 110 c.c. capacity, which has a wide neck fitted with a rubber stopper containing two holes. One hole is provided with a short glass tube bent at right angles, and the other with a longer tube, reaching nearly to the bottom of the bottle and connected by means of rubber tubing with the bulb B, of 70 c.c. capacity, and fitted with valves

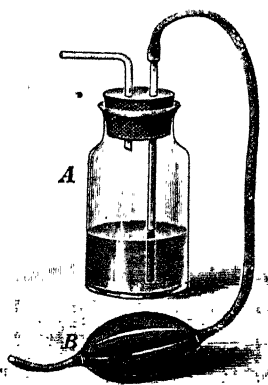


FIG. 200.

<sup>1</sup> *Z. angew. Chem.*, 1888, 1, 395; 1889, 2, 12.

which allow the air to pass through in one direction only. The bottle is first filled with the air under examination by compressing and relaxing the bulb several times in succession; 10 c.c. of the dilute reagent are then quickly poured into the bottle and the contents of the bulb slowly driven through the liquid, which is shaken for one minute. Meanwhile the bulb refills with air; a second portion of air is then blown through and the bottle again shaken for one minute, and this process repeated until the red colour of the indicator changes to a pale yellow. If the carbon dioxide content of the air under examination is considerable, from 2 to 4 compressions of the bulb suffice to effect the change of colour, whilst with fresh air from 30 to 40 deliveries may be necessary. Lunge and Zeckendorf have constructed the following table, which gives the carbon dioxide content of the air from the number of compressions of the bulb, for a sodium carbonate solution of the strength given above ( $N/500$  sodium carbonate solution).

No. of Compressions.	Carbon dioxide content, in parts per thousand.	No. of Compressions.	Carbon dioxide content, in parts per thousand.
2	3.00	15	0.74
3	2.50	16	0.71
4	2.10	17	0.69
5	1.80	18	0.66
6	1.55	19	0.64
7	1.35	20	0.62
8	1.15	22	0.58
9	1.00	24	0.54
10	0.90	26	0.51
11	0.87	28	0.49
12	0.83	30	0.48
13	0.80	35	0.42
14	0.77	40	0.38

The method becomes very tedious when the air is pure, as even with 0.5 parts of carbon dioxide per thousand the shaking must be continued for twenty-six minutes for a single estimation; on the other hand, if the proportion of carbon dioxide approaches from 1 to 3 parts per thousand, which may frequently occur in crowded rooms, the method is very suitable. With less pure air, Lehmann and Fuchs<sup>1</sup> found that a solution of sodium carbonate, twice as concentrated as that given above was more suitable and gave more accurate results. In using this stronger solution:—

16 Compressions = 1.2 per cent.

8 " = 2.0 "

7 " = 2.2 "

6 " = 2.5 "

5 Compressions = 3.0 per cent.

4 " = 3.6 "

3 " = 4.2 "

2 " = 4.9 "

H. Wolpert<sup>2</sup> has also devised an apparatus depending upon the same

<sup>1</sup> *Z. angew. Chem.*, 1899, 12, 620.

<sup>2</sup> *Arch. f. Hygiene*, 27, 291.

principle, which offers the advantage that the test can be made secretly, as the apparatus, which is shaped like a syringe, is only 20 cm. long and 3 cm. in diameter. The total volume of air, however, that can be examined is only 50 c.c., and only 2 c.c. of a very dilute sodium carbonate solution can be used for the absorption of the carbon dioxide. Wolpert made use of this apparatus in the examination of the air in clothing, the sample being taken by piercing the sharp nozzle of the tube through the cloth.

#### 4. Aqueous Vapour.

The quantity of aqueous vapour present in air is very variable, and is influenced by several factors, especially by the temperature. At any given temperature air is capable of taking up a definite amount of aqueous vapour per cubic metre; this quantity, expressed in grams, is called the *maximum humidity*. Between the temperatures of 7° and 30° C., the maximum humidity is approximately the same as the temperature expressed in degrees centigrade; also the tension of aqueous vapour expressed in mm. of mercury is almost identical with the maximum humidity.

#### Maximum Moisture Content in 1 cb.m. of Air in grams.

*Maximum Vapour Tension of Water in mm. of Mercury at different Temperatures of the Air.*

Tempera- ture.	Vapour Tension.	Grams of Water.	Tempera- ture.	Vapour Tension.	Grams of Water.	Tempera- ture.	Vapour Tension.	Grams of Water.
-10°	2.0	2.1	8°	8.0	8.1	21°	18.5	18.2
- 8	2.4	2.7	9	8.5	8.8	22	19.7	19.3
- 6	2.8	3.2	10	9.1	9.4	23	20.9	20.4
- 4	3.3	3.8	11	9.8	10.0	24	22.2	21.5
- 2	3.9	4.4	12	10.4	10.6	25	23.6	22.9
0	4.6	4.9	13	11.1	11.3	26	25.0	24.5
1	4.9	5.2	14	11.9	12.0	27	26.5	25.6
2	5.3	5.6	15	12.7	12.8	28	28.1	27.0
3	5.7	6.0	16	13.5	13.6	29	29.8	28.6
4	6.1	6.4	17	14.4	14.5	30	31.6	30.1
5	6.5	6.8	18	15.2	15.1	50	...	83.4
6	7.0	7.3	19	16.3	16.2	70	...	199.8
7	7.5	7.7	20	17.4	17.2			

The term *absolute humidity* denotes the quantity of water, in grams, which is present in 1 cb.m. of air. The percentage ratio of the absolute humidity to the maximum value is called the *relative humidity*. The difference between the maximum and the absolute humidity is sometimes called the *deficit of saturation*.

An alternative method of stating the humidity is to express the vapour tension of the contained aqueous vapour in mm. of mercury;

a distinction may be similarly drawn between *maximum*, *absolute*, and *relative* vapour tension, and *difference of vapour tension*.

For the determination of the absolute humidity, a useful method is to pass measured volumes of air through two small flasks placed in series, and containing pumice which has been previously heated and then saturated with concentrated sulphuric acid, and to determine the increase in weight. The flasks are provided with ground-glass stoppers or corks; if cork is used, it should be covered with sealing-wax. For most purposes, a sufficiently accurate result can be obtained by simply passing the air through two flasks containing concentrated sulphuric acid. The increase of weight from a litre of air varies from 2 mg. to a maximum limit of 25 mg.

Physical methods are employed more frequently than chemical methods for the determination of the amount of moisture. Of these the method based upon the difference between the readings of a dry- and wet-bulb thermometer (August's *Psychrometer*), is sufficiently accurate for all practical purposes. For this determination, two good mercury thermometers, graduated in tenths of degrees, and which must read together at all parts of the scale, are supported on a stand. A layer of thin muslin is tied round the bulb of one of the thermometers, and is joined to a strip of muslin pleated together in the form of a wick, which dips into a small vessel of water. The apparatus is exposed for a time to the air under examination, the temperatures registered by the two thermometers read off, and the difference between the two readings noted. If  $t_s$  be the temperature of the dry bulb,  $t_h$  that of the wet bulb,  $f_{t_s}$  the maximum humidity at the temperature of the dry bulb, as given in the above table (p. 877), and  $c$  a constant, which has the value 0.65 at temperatures above  $0^\circ$  C. and 0.56 at temperatures below  $0^\circ$ , the absolute humidity  $a$  is calculated from the formula:—

$$a = f_{t_s} - (t_s - t_h)c.$$

The values determined by August for the constant are somewhat too low for air, in a state of rest, in rooms; it is better to assume  $c$  to be equal to 0.8 to 0.9, otherwise the values obtained for the absolute humidity are too high.

The hygrometric tables prepared by Glaisher<sup>1</sup> can be advantageously used for calculating the absolute and relative humidity from the readings of the two thermometers.

An improved form of psychrometer, which is, however, only made use of in more accurate work, is obtained by suspending each of the thermometers by means of an eyelet with a pleated cord, so that the distance from the thermometer bulbs to the point at which the cord is

<sup>1</sup> *Hygrometrical Tables*, by J. Glaisher, published by Taylor & Francis, Red Lion Court, Fleet Street, London.

fixed is exactly 1 metre. The bulb of the wet-bulb thermometer is covered with a double layer of muslin. For the determination, the dry-bulb thermometer is first swung in a circle, so that each revolution takes exactly one second, and after 100 swings the temperature quickly observed. The same procedure is then repeated with the wet-bulb thermometer, the bulb having been first dipped into water. The thermometer scales are usually divided in fifths of a degree to facilitate reading from a distance. The vapour pressure (absolute tension) is calculated from the formula:—

$$d_a = d_{t_s} - 0.000706 \times b \times t_s - t_h$$

in which  $b$  is the barometric pressure,  $d_a$  the absolute vapour pressure, and  $d_{t_s}$  the vapour pressure at the temperature  $t_s$  of the dry-bulb thermometer.

Satisfactory determinations of the moisture in air can also be made with a good hair hygrometer. The readings of the hair hygrometer must always be checked before use by comparison with a psychrometer, or preferably, with the results of a chemical determination. The readings only give the relative humidity, from which the absolute humidity can be calculated from the equation:—

$$\frac{mr}{100} = a$$

in which  $m$  is the maximum humidity for the temperature of the air,  $r$  the relative humidity, and  $a$  the absolute humidity.

If only isolated determinations of the humidity are required, and accurately calibrated instruments are not available, the direct weighing of the water content of the air is always the most reliable method.

The calculation of vapour tension to absolute humidity, and *vice versa*, is carried out as follows:—

$$\text{Absolute humidity} = \frac{\text{Vapour tension}}{1 + 0.00366 t} \times 1.06.$$

$$\text{Vapour tension} = \text{Absolute humidity} \times \frac{1 + 0.00366 t}{1.06}$$

### 5. Hydrogen Peroxide.

The investigations of Schöne<sup>1</sup> have proved that hydrogen peroxide is an almost constant component of fresh air, although often only present in very minute quantities. It is most easily detected in rain water, which is collected for this purpose in porcelain or glass vessels. The quantity present in snow is relatively small, since the hydrogen peroxide content of the air has its maximum in summer and its minimum in winter. According to Schöne, 0.05—0.06 mg. in 1 litre of rain water is a small proportion, 1 mg. per litre an unusually high content. The

<sup>1</sup> *Z. anal. Chem.*, 1894, 33, 137.

hydrogen peroxide content of the air itself is very small; Schöne gives as a maximum 0.57 mg. in 1000 cb.m.

Of the reactions for hydrogen peroxide, the following three are of special importance:—

1. The blue coloration with chromic acid. A trace of potassium bichromate is added to the solution containing the hydrogen peroxide, which is then covered with a layer of ether, and the whole shaken with a trace of sulphuric acid. The resultant blue perchromic acid imparts an intense colour to the ether. The quantity of bichromate added must be less, the smaller the quantity of hydrogen peroxide present. The quantity of hydrogen peroxide present in rain water is never sufficient to give this conclusive reaction.

2. The blue coloration with potassium iodide and starch on addition of ferrous sulphate (Schönbein). If rain water remains colourless on addition of potassium iodide and starch, prepared according to the directions given below, but becomes blue on addition of very little ferrous sulphate, the presence of hydrogen peroxide is proved (Schöne). Twenty-five c.c. of the rain water, which has not been acidified, is treated with 1 c.c. of a 5 per cent. potassium iodide solution and 2 to 3 c.c. of starch solution. No blue coloration should result before the addition of the ferrous sulphate, although a coloration results, without this addition, after standing for several hours. The test is then completed by the addition of a drop or a few drops of a 0.5 per cent. solution of ferrous sulphate, as little as possible being added.

The addition of acid, of much starch, or of much ferrous sulphate affects the sensitiveness of the reaction. The starch solution is prepared, according to Schöne, as follows:—1 g. of the purest starch in small pieces is shaken in a test-tube with from 20 to 25 c.c. of distilled water, allowed to subside for from one to two minutes, and the starch which remains suspended decanted into from 400 to 500 c.c. of boiling water; the solution is then boiled for one minute and allowed to cool. The method can be made approximately quantitative by a colorimetric comparison with known quantities of hydrogen peroxide. If larger quantities are present, the liberated iodine can be titrated with sodium thiosulphate; 1 c.c. of *N*/10 sodium thiosulphate = 3.4 mg.  $\text{H}_2\text{O}_2$ .

3. As a further method, Schöne recommends the guaiacol-malt extract test, previously used by Schönbein; provided certain sources of error and precautions are taken into account, very good results are obtained.

The materials required are:—(i.) A fresh solution of guaiacol prepared by dissolving 2 g. of guaiacol resin fragments, taken from the interior of a sample which has been kept in the dark, in 100 c.c. of 96 per cent. alcohol which has not previously stood in sunlight. Guaiacol which has been exposed to light first becomes blue and then brown, and loses the property of turning blue with hydrogen peroxide; alcohol

which has been exposed to light gives the hydrogen peroxide reaction. Old guaiacol solutions give a bluish green coloration in absence of hydrogen peroxide. (ii.) A freshly prepared diastase solution. Since pure, dry diastase, which is not affected by keeping, can be bought, it is not necessary to prepare an extract of malt.

The solution to be tested should be very faintly alkaline, or in any case not acid. One hundred c.c. are treated with 1 c.c. of the guaiacol solution and 0.5 to 1 c.c. of the diastase solution, and allowed to stand for a few minutes; a more or less intense bright blue coloration indicates the presence of hydrogen peroxide. If the experiment is carried out in this way, the coloration soon reaches its maximum, and then gradually fades away. Neutral ammonium nitrite does not give this reaction.

### 6. Ozone.

Ozone is present only in traces in the air, and all the older data as to its quantitative estimation are unreliable, as the reactions employed were ambiguous and uncertain. In particular, it is now generally recognised that the blue coloration of acidified potassium iodide-starch solution is neither a qualitative nor quantitative indication of the presence of ozone. Chlorine, bromine, and especially nitrites, which occur frequently in the air, colour acidified potassium iodide and starch; chlorine and bromine also colour neutral solutions, whilst light and sulphuretted hydrogen both effect a decolorisation.

The immediate blue coloration of a neutral solution of potassium iodide and starch might serve as a certain test for ozone, in absence of chlorine, since the colour forms only very slowly in presence of hydrogen peroxide, and not at all with nitrites.

According to Engler and Wild,<sup>1</sup> the following test is a reliable proof of the presence of ozone:—Large quantities of the air under examination are first passed through finely divided chromic acid to remove the hydrogen peroxide, and then into a glass tube in which are placed, side by side, a manganese sulphate paper, which is coloured brown by ozone, but not by chlorine (formation of  $Mn_3O_4$ ), and a thallos oxide paper, which remains colourless in presence of nitrous acid, but is turned brown by ozone. If both papers are coloured, ozone is present.

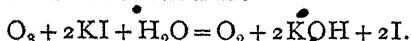
Various colour reactions with organic compounds have been proposed for the qualitative detection of ozone, of which that with tetramethyldi-*p*-diaminodiphenylmethane is the most definite and distinctive.<sup>2</sup> This reagent, which is known as "tetramethyl base," is used, either in alcoholic solution or as a test paper. Ozone produces a violet coloration and nitrogen oxides a straw yellow; hydrogen peroxide gives no reaction.<sup>2</sup>

<sup>1</sup> *Ber.*, 1896, 29, 1940.

<sup>2</sup> Cf. Arnold and Mentzel, *Ber.*, 1902, 35, 1324, 2902; F. Fischer and H. Marx, *ibid.*, 1906, 39, 2555.



It is scarcely possible to give a reliable method for the estimation of ozone in the air. The following data were recently obtained by Hatcher and Arny: <sup>1</sup>—February, 0.015 to 1.12 mg.; March 0.08 to 15.81 mg. in 100 litres of air. The titration of the iodine set free from potassium iodide by sodium thiosulphate can certainly be used in the case of pure air, to which ozone has been added artificially, but the process is open to objection for impure air. The potassium iodide solution must in any case not be acidified. The reaction is:—



One c.c. *N*/1000 sodium thiosulphate solution (0.2483 g. per litre = 0.024 mg.  $\text{O}_3$ ).

### 7. Ammonia.

Ammonia, which is almost always found in traces in the atmosphere, results chiefly from the putrefaction of organic substances containing nitrogen and from the decomposition of urea.

It may be detected qualitatively by sensitive litmus or turmeric paper, which is fixed between glass plates or watch-glasses so that only the projecting portion, which is moistened with water free from ammonia, is exposed to the air to be examined. The enclosed part of the paper serves as a comparison and forms a good means of detecting very slight alterations in the colour of the exposed portion. Hæmatoxylin paper is also useful for the detection of very small traces of ammonia. It is prepared by steeping freshly macerated logwood in alcohol, and soaking strips of white paper in the tincture; the yellow colour of the paper is turned to red-violet or violet-blue by ammonia. Paper which has been saturated with Nessler's reagent (p. 765) is still more sensitive.

For the quantitative estimation of considerable quantities of ammonia, the air is passed through 20 c.c. of an *N*/10 or *N*/20 solution of sulphuric or hydrochloric acid. Litmus, rosolic acid, or methyl orange is used as indicator, but not phenolphthalein. (*Cf.* p. 71.)

If the ammonia content is very small, the air is passed through water slightly acidified with sulphuric acid, and the absorbed ammonia estimated colorimetrically by Nessler's reagent (p. 765). In the Montsouris Observatory <sup>2</sup> the Duboscq colorimeter is used for the colour comparison.

### 8. Nitrous (and Nitric) Acid.

Nitrous acid is a constant component of the air, but is present in very minute quantities. According to Schöne, <sup>3</sup> the air always contains three times as much ammonia as nitrous acid. Defren <sup>4</sup> found 0.014 mg. of  $\text{N}_2\text{O}_5$  in 10 litres of fresh air, and 0.07 mg. in 10 litres of the air of a room

<sup>1</sup> *Amer. J. Pharm.*, 1900, p. 423.

<sup>2</sup> *Bulletin de l'Observatoire de Montsouris*, 1871, p. 505.

<sup>3</sup> *Z. anal. Chem.*, 1894, 33, 141.

<sup>4</sup> *Chem. News*, 1896, 74, 240.

in which lights were burning. It is best determined in rain water, according to the method given in the section on "Drinking Water and Water Supplies," p. 759. For its determination in the air, large quantities of air (100 litres or more) are passed through dilute potassium hydroxide solution, and the resulting nitrite estimated. The method gives somewhat low results, for, as Lunge<sup>1</sup> has shown, some nitrous acid is always decomposed to nitric acid and nitric oxide. It has therefore been considered sufficient<sup>2</sup> to pass the air through flasks cooled with ice and to estimate the nitrous acid in the water which condenses, or to pump from 8 to 9 litres of the air into a bottle, add 100 c.c. of water, and allow the whole to stand for twenty-four hours.<sup>3</sup> As oxidation easily occurs during this latter method of estimation, it is advisable to estimate the total combined nitrogen acids as described on p. 817.

All apparatus and reagents used in these estimations must, of course, be carefully tested beforehand, to ensure the absence of nitrates and nitrites.

The estimation of larger quantities of nitric oxide, nitric trioxide, and nitric peroxide is described in the section on "Sulphuric Acid" (pp. 328 and 332). Their determination is usually effected either with potassium permanganate, or, if the quantity is small, colorimetrically. (Cf. pp. 377 and 379).

## II.—THE ESTIMATION OF THE IMPURITIES IN THE AIR OF TOWNS AND OF CONFINED SPACES

The examination of air for the presence of gases other than oxygen, nitrogen, and carbon dioxide, requires considerable care, as they are usually present only in very small quantities, and it is accordingly necessary to deal with large volumes of air for their estimation.

The most convenient laboratory method for aspirating the samples is by means of an ordinary water-pump, the volume of gas being measured by an ordinary gas meter. Or the gas meter itself may be employed as the aspirator by fixing a series of cog-wheels to the axle of the drum and driving these, either by means of a falling weight, or preferably with a small electric motor; this plan has been advantageously used for the estimation of sulphur dioxide in air. (Cf. Fig. 201, p. 885.) If smaller quantities of air are required, or if the sample is collected in the open or in a confined space in which the above methods are not available, the aspiration is best effected by running water out of glass, metal, or wooden vessels which are connected by suitable means to the apparatus employed for the estimation; the volume of air

<sup>1</sup> *Dingl. polyt. J.*, 1879, 233, 240.

<sup>2</sup> E. Cramer, *Arch. f. Hygiene*, 10, 324.

<sup>3</sup> Defren, *Chem. News*, 1893, 74, 240.

aspirated is obtained either by calibrating the vessel used, or by measuring the volume of water run off.

If it is only required to obtain qualitative indications of the presence of a gas in air, or if the quantity is so small that a quantitative determination is out of the question, test papers soaked with suitable indicators, *e.g.* litmus, lead nitrate, palladious chloride, etc., may be employed as a means of identification. An alternative method recommended by Ost<sup>1</sup> and also by Wislicenus is to suspend sheets of cloth, soaked in suitable absorbents, such as baryta water, in the air, and subsequently to test for absorbed gases such as hydrofluoric acid, sulphurous acid, hydrochloric acid, etc.

For quantitative determinations absorption vessels of the most varied form are in use, such as U-tubes, Peligot's tubes, Will-Varentrapp pear-shaped absorption tubes, and Lunge's 10.-bulb absorption tube (Fig. 127, p. 338). Lehmann recommends tubes of a form suggested by Rosenthal, about 30 cm. long, 1.8 cm. diameter, and widened at the upper end to 2.5 cm., which hold about 25 c.c. of the reagent; they are fitted with glass stoppers through which two glass tubes pass, one cut off short within the tube and the other drawn out to a fine capillary. For quantitative determinations, two absorption vessels should always be connected in series, and the air, as it leaves the second vessel, should be carefully tested qualitatively for traces of the gas which is being determined. When small quantities of a gas are to be measured and the estimation is to be made by titrating back the excess of the absorbent, as is usually the case, it is well to use the reagents as dilute as possible, as greater accuracy is thereby obtained.

### 1. Sulphurous Acid.

The injurious action of sulphurous acid in air on vegetation has long been recognised, and the relation of its presence to the mortality from respiratory diseases during foggy weather has become particularly emphasised by recent investigations on the quantities present in the air of large towns;<sup>2</sup> also it has a very destructive effect upon certain kinds of building stone, after being oxidised to sulphuric acid.<sup>3</sup> It originates entirely from the combustion of fuel, a portion of the contained sulphur being oxidised during combustion to sulphur dioxide, which undergoes further oxidation to a greater or less extent in the atmosphere, to sulphuric acid.

The proportion of sulphur compounds present in the air of large towns, under varying atmospheric conditions, is indicated by the follow-

<sup>1</sup> *Chem. Ind.*, 1900, 23, 292.

<sup>2</sup> Cf. "The Atmosphere of Manchester," Report to the Manchester Field Naturalists' Society, 1891; "Town Fogs and their Effects," W. J. Russell, *Nature*, 1891, 45, ii.; "The Effects of Urban Fogs upon Cultivated Plants," F. W. Oliver, *J. Royal Horticultural Society*, 1893, 16, 1.

<sup>3</sup> Cf. A. H. Church, *Nature*, 1907, 76, 110.

ing data obtained in series of analyses made during the years 1890 to 1895 in London, Manchester, and Liverpool; the results are expressed in volumes of  $\text{SO}_3$  per million volumes of air:

In clear weather, 0.1 to 0.5.

Hazy weather during winter months, 2 to 5.

Slight fog, 2 to 10.

Dense fog, 10 to 20.

A maximum of 38.1 was obtained during a dense fog at St. Bartholomew's Hospital, London, during December 1892.

The apparatus used in these determinations was devised by G. H.

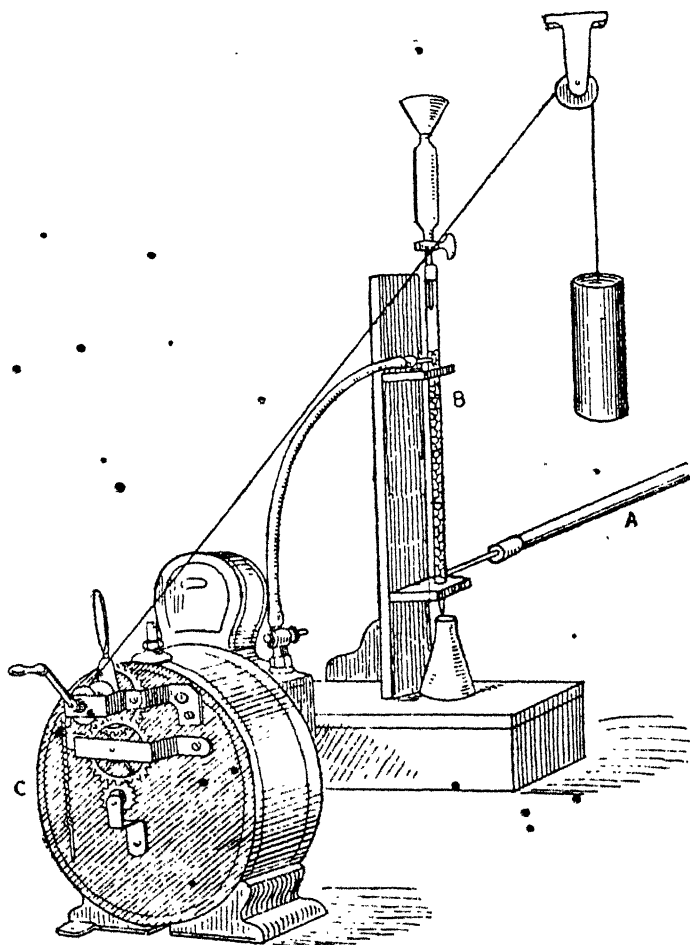


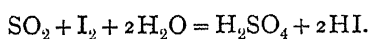
FIG. 201.

Bailey in connection with the work of the Air Analysis Committee of the Manchester Field Naturalists' Society, and is shown in Fig. 201.

The inlet tube A, of about 12 mm. diameter, is fixed horizontally so as to project into the open air. The glass tower B is about 75 cm. high and 3 cm. in diameter, and is provided with inlet and outlet tubes on opposite sides, as shown; a tap-funnel is fitted into the top of the tower by means of a good cork, and the tower itself is filled with glass beads to within 25 cm. of the upper side tube. This latter tube is connected by a piece of rubber tubing, to the wet meter C, which serves also as the aspirator, a set of toothed wheels being attached, as shown, which are driven by the falling weight. As mentioned above, a small electric motor can be advantageously substituted for driving the meter.

To carry out a determination, the tap-funnel is charged with about 250 c.c. of a solution of hydrogen peroxide containing about 1 mg. of active oxygen per c.c., which is allowed to drip through the tower at a rate of about 1 drop a second, whilst the sample of air is aspirated through; the liquid drips through to the flask placed below, and as the jet is quite sealed by the solution, the entrance of air from the interior of the room is effectually avoided. After the whole of the solution has passed through, it is poured back into the funnel and again run through the tower. The air is aspirated at the rate of from 20 to 30 cubic feet per hour, and from 50 to 100 cubic feet should be drawn through for a determination, according to the quantity of sulphur dioxide likely to be present. After sufficient air has been passed through, the tap-funnel and tower are carefully washed out, and the sulphuric acid in the total solution determined gravimetrically as barium sulphate in the usual way.

Lehmann gives the following method for the quantitative determination of sulphur dioxide in air:—As large a quantity of air as possible is passed through 20 c.c. of a standardised *N*/10 solution of iodine; the reaction takes place in accordance with the equation (*cf.* p. 116):—



As a precaution against loss of iodine a second absorption vessel containing 5 c.c. *N*/10 sodium thiosulphate solution is placed behind the flask containing the iodine. After the requisite volume of air has been passed through the flasks the iodine and thiosulphate solutions are mixed together, and the excess of the iodine solution titrated back with sodium thiosulphate; 1 c.c. of the thiosulphate solution corresponds to 3.2 mg. of sulphur dioxide. If only very small quantities of sulphur dioxide are present it is advantageous to use *N*/50 solutions.

Haldane<sup>1</sup> uses two test tubes for the absorption charged respectively with 10 c.c. of *N*/100 iodine solution and *N*/100 sodium arsenite

<sup>1</sup> *Report on the Composition of the Air in the Metropolitan and other Railway Tunnels*, 1897, published by Eyre & Spottiswoode, London.

solution; a definite volume (16.5 litres) of the air is drawn through the tubes by means of a large aspirator at the rate of about 120 c.c. per minute, and the excess of arsenite titrated back with iodine after mixing the contents of the two tubes.

Sulphur dioxide can also be absorbed with sodium hydroxide, and determined, after oxidation, as barium sulphate.

These methods fail in some cases, especially when the sulphurous acid is only evolved intermittently, or when it passes into the air in very minute quantities. In winter, the difficulty may be overcome by collecting samples of snow from the district under examination, and at other times by examining deposits from the roofs of buildings such as greenhouses, or from the leaves of outdoor plants. The sample of snow taken should be uniform throughout its thickness. About 1 kilo is melted over a spirit lamp (the combustion products from gas flames contain sulphur dioxide), filtered, and 500 c.c. of the clear solution oxidised, to convert the sulphurous into sulphuric acid, which is then determined as barium sulphate. It is advisable to carry out the determinations soon after the snow has fallen, and, if possible, to repeat it after successive intervals of time; also control determinations on samples taken from different localities are necessary, since the direction of the wind may affect the results to a surprising extent.

The following results of determinations of the sulphur compounds in snow and in deposits are taken from the Report of the Air Analysis Committee of the Manchester Field Naturalists' Society (1891):—

	Mg. SO <sub>2</sub> per sq. m. of Surface.
Fresh-fallen snow near the centre of the city (Royal Infirmary)	10
Same deposit and locality after 1 day	19
" " " 3 days	31
Snow outside centre of city (Owens College) after 1 day	5.2
Same deposit and locality after 2 days	21
Snow further away from centre of city (Fallowfield) after 1 day	4.3
Same deposit and locality after 3 days	7.5

Deposits on aucuba leaves in mg. per sq. m. of leaf surface:—

	Total Solid Deposit.	Sulphuric Acid.	Hydrochloric Acid.
Royal Infirmary	568	18.3	14.1
Owens College	315	10.4	17.3

Deposits collected from the roofs of greenhouses at Chelsea and at Kew in February 1891, during severe fogs contained 4.33 and 4.0 per cent. of sulphuric acid respectively.<sup>1</sup>

<sup>1</sup> F. W. Oliver, *loc. cit.*

Lehmann gives the following data:—

	Mg. SO <sub>2</sub> per Kilo.
Snow (3 days old) from the Botanic Garden, Würzburg . . .	6.3
" " " " centre of the town . . .	31.3
" " " " from the yard of a cellulose works . . .	72.8

## 2. Hydrogen Sulphide.

Hydrogen sulphide may be detected qualitatively in very great dilution by its characteristic smell; the smell is less distinctive if the proportion exceeds about 0.1 per cent., but its presence is then indicated by the irritation produced on the eyes, a warning symptom which should never be neglected on account of the very poisonous nature of the gas (Haldane). It may also be easily recognised by exposing strips of lead acetate or nitrate paper, but it should be borne in mind that traces of black lead sulphide are gradually converted into lead sulphate.

Minute quantities of hydrogen sulphide in air may be detected colorimetrically as follows:—A strip of filter paper, 5 cm. long and 2 cm. broad, is soaked in lead nitrate solution and introduced into the mouth of a glass tube, 30 cm. long and 12 mm. in diameter, and the sample of air passed through the tube at a velocity of 6 litres in thirty minutes. If only a pale yellowish brown coloration is formed after passing 8 litres of air, the quantity of hydrogen sulphide present in the air is about 1 to 2 volumes per million. Even this quantity is sufficient to impart a very disagreeable smell to the air. A strong yellowish brown colour corresponds to about three parts per million, a dark brown colour to five, and a brownish black colour to eight parts. This method is to be recommended especially when a continuous control has to be kept over pollution of the air by waste gases from works.<sup>1</sup>

Larger quantities of hydrogen sulphide are readily determined iodometrically. (*Cf.* p. 116.) The air is passed through an *N/10* iodine solution, and the quantity of iodine used up by the hydrogen sulphide ascertained by titrating back with *N/10* sodium thiosulphate solution; 1 c.c. corresponds to 1.7 mg. H<sub>2</sub>S.

## 3. Hydrochloric Acid.

The hydrochloric acid in air is determined by absorption with 5 or 10 per cent. sodium hydroxide solution, free from chloride; from 20 to 50 litres of air should be used for the estimation. The alkaline solution is subsequently neutralised with nitric acid and the contained chloride estimated by titration either with silver nitrate and ammonium thiocyanate (*cf.* p. 123), or with silver nitrate directly, using potassium

<sup>1</sup> *Cf.* Lehmann, *Arch. f. Hygiene*, 14 and 30.

chromate as indicator (*cf.* p. 123); Lehmann gives preference to the former method. Quantities of hydrochloric acid, sufficiently large for determination by direct acidimetric means, are seldom found in the air. The results of determinations of the quantity of hydrochloric acid found in deposits on aucuba leaves in Manchester have been given above, p. 887; the deposits collected from the roofs of greenhouses at Chelsea and at Kew contained 1.43 and 0.83 per cent. of hydrochloric acid respectively.

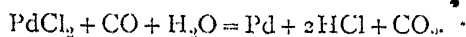
#### 4. Carbon Monoxide.

Carbon monoxide may occur in the air of closed rooms as a product of the incomplete combustion of fuel, or it may be present as the result of leakage of gas supplies; illuminating gas contains from 4 up to 18 per cent. of carbon monoxide according to the proportion of carburetted water-gas admixed with ordinary coal gas. It is also found in the air of underground railways, as a product of incomplete combustion, and in the air of mines where, except in a few exceptional cases, it is invariably produced either by fire or by heating.

Carbon monoxide is an extremely poisonous gas, and the detection of small quantities is accordingly of great importance. Haldane<sup>1</sup> has shown that nearly all the deaths in colliery explosions and in underground fires in mines are due to the carbon monoxide contained in the after-damp.

The detection and approximate quantitative estimation of small quantities of carbon monoxide can be effected either by its reducing action on palladious chloride or by its action upon blood; in the latter case the change produced is examined either spectroscopically or colorimetrically. The flame-cap test is also applicable. Other methods are available for the determination of larger quantities of the gas.

• **The Palladious Chloride Test.**—Palladious chloride is reduced to metallic palladium by carbon monoxide, according to the equation:—



For the qualitative detection of carbon monoxide, test papers are prepared by soaking narrow strips of filter paper in a solution of palladious chloride containing 0.2 mg. in 1 c.c. of water and dried. A strip is then moistened and suspended in a bottle containing some water, and into which 10 litres of the air to be examined have been passed; the bottle is then corked and allowed to stand. 0.5 parts of carbon monoxide per 1000 of air produce a brilliant black film on the surface of the paper in a few minutes; 0.1 parts per 1000 give the same result after from two to four hours, whilst smaller quantities require a considerably longer time. Hydrogen sulphide and ammonia

<sup>1</sup> *Causes of Death in Colliery Explosions.* J. Haldane. Blue Book [C. 8112], 1896. Published by Eyre & Spottiswoode.



must be absent for this test, which is also open to the objection that acetylene and other hydrocarbons reduce palladious chloride.

The test can also be carried out by first absorbing the carbon monoxide with blood, and then trying its reducing action according to the following method proposed by Fodor:<sup>1</sup>—The blood solution, which has been shaken with the air suspected to contain carbon monoxide, is introduced into a flask with a double-bored cork, which is placed on a boiling water-bath. The flask is connected on the inlet side with a wash-bottle containing palladious chloride, and on the outlet side with a series of absorption vessels, of which the first contains sulphuric acid, the second lead acetate, and the third and fourth palladious chloride. A very slow current of air is aspirated slowly through the whole apparatus. The wash-bottle removes any traces of carbon monoxide or of other substances which reduce palladious chloride from the air. The current of air then takes up the gases liberated from the boiling blood solution, of which ammonia and hydrogen sulphide are retained by the sulphuric acid and lead acetate, whilst the carbon monoxide passes on to the two palladious chloride absorption vessels. The heating of the blood and the aspiration of the air must be continued for at least half an hour. According to Fodor, it is possible by this method to detect 0.2 parts per 1000 of carbon monoxide in the air. Klepsoff<sup>2</sup> found that in this method, a considerable portion of the carbon monoxide removed from the blood by the air, passes unchanged through the palladious chloride solution, and is thus lost; he states that the test can be made much more sensitive if the absorption apparatus containing the palladious chloride is replaced by a series of funnels, hermetically sealed and fitted with filter papers soaked with palladious chloride.

**The Spectroscopic Test.**—Carbon monoxide is very readily absorbed by blood, even when present in only very small quantities; it displaces the oxygen of the oxyhæmoglobin of the blood and forms carboxyhæmoglobin, the absorption spectrum of which is characteristically different from that of oxyhæmoglobin. The carbon monoxide is absorbed from the air to be examined, either by shaking a volume of the air with a solution of blood, or by placing mice or rats in the air, and subsequently withdrawing a portion of their blood for the test; it is impossible to absorb the gas by passing a current of air through a solution of blood.

The spectroscopic examination is best carried out in the following way:<sup>3</sup>—100 c.c. of fresh defibrinated blood are diluted with about 50 c.c. of water and poured into a bottle of from 6 to 10 litres capacity, previously filled with the air to be examined. The bottle is then

<sup>1</sup> *Deutsch. Viertelj. f. öff. Gesundheitspflege*, 1880, 12, 377.

<sup>2</sup> *Researches of the Hyg. Lab. of the University of Moscow*, 1886,

<sup>3</sup> *Cf. Vogel, Ber.*, 1877, 10, 794; 1878, 11, 235.

closed, with a rubber cap and carefully shaken from time to time for half an hour, so as to allow the blood to absorb as much carbon monoxide as possible. In presence of carbon monoxide the blood is turned a pink colour, which is very characteristic and easily recognised if compared with the colour of the original blood solution.

Ten drops, both of the normal blood and of that which has been shaken with the air, are then diluted to about 20 c.c., and examined in the spectroscope. Oxyhæmoglobin (normal blood) shows two absorption bands with sharp edges in the yellow and green, between the Fraunhofer lines D and E. In presence of carboxyhæmoglobin these bands also appear, but lie closer together and have indistinct borders. The difference is rendered more distinct by treatment with reducing agents, such as ammonium sulphide or ferrous ammonium tartrate (Stokes' solution); to prepare the latter, ferrous sulphate is dissolved in water, and solid tartaric acid added until a dense precipitate results, which is dissolved by adding excess of ammonia, when a black-green solution is formed, which must be kept in well-stoppered bottles. A few drops of the reducing agent are added to each solution. Oxyhæmoglobin is reduced at once to hæmoglobin, but the more stable carboxyhæmoglobin is not affected. The hæmoglobin formed gives one ill-defined absorption band, which not only takes up the interval between the two absorption bands of the unaltered oxyhæmoglobin, but extends further on either side, but not so far as the Fraunhofer lines D and E; carboxyhæmoglobin, on the other hand, shows the two indistinct bands almost unaltered. According to Vogel, a carbon monoxide content of 2.5 parts per 1000 in air can be detected in this way. This method is very useful for the detection of carbon monoxide in the blood in cases of poisoning by the gas. It can also be applied to the detection of carbon monoxide in tobacco smoke by blowing smoke for a time through a bottle of 200 c.c. capacity.

Since blood is never quite saturated with carbon monoxide and always contains oxyhæmoglobin at the same time, the bands of the carboxyhæmoglobin are generally more or less obscured by superimposed bands of the reduced hæmoglobin. From the relative intensity of the bands of carboxyhæmoglobin and of the reduced hæmoglobin, it is possible, with some practice, to determine approximately the degree of saturation of the blood with carbon monoxide.<sup>1</sup> Uffelmann has shown that the indications are sharper if about 10 per cent. of sodium hydroxide solution is added to the blood after the addition of the ammonium sulphide. The spectrum of the carboxyhæmoglobin still remains unaltered, whereas the reduced hæmoglobin is converted into hæmchromogen, which gives a sharp, dark absorption band between D and E (nearer to D), and an indistinct band at E. If the

<sup>1</sup> Cf. Uffelmann, *Arch. f. Hygiene*, 1884, 2, 207.

Blood is only partially saturated with carbon monoxide, hæmochromogen and carboxyhæmoglobin are both indicated. Uffelmann was able to detect 0.33 parts per 1000 of carbon monoxide in air by this method.

**Colorimetric Test.**—The colorimetric comparison of the tint of a solution of blood containing carbon monoxide with that of a normal blood solution forms a certain and extremely delicate test for the detection of the gas, which is both simpler and more sensitive than the spectroscopic examination. This test is due to J. S. Haldane,<sup>1</sup> who has worked out the necessary details with great care.

A very dilute solution of normal blood, which may be obtained from a prick in the finger, is first prepared, which should be of such dilution that the solution has a yellow tinge. Portions of this solution are placed in each of two test tubes of equal diameter, and the solution in one of them thoroughly shaken up with ordinary coal gas until the hæmoglobin is saturated with carbon monoxide, when its colour changes to pink. The air to be examined is tested by introducing a mouse into it and then placing a drop of its blood, which may easily be obtained by opening the heart, into a test tube of the same diameter as those used for the normal blood, and diluting the blood cautiously until the *depth* of tint is equal to that of the other two solutions. The solution thus obtained will be intermediate in colour between that of the blood saturated with carbon monoxide and that of the normal blood, and will approach the one or the other according to the percentage of carbon monoxide in the air tested; an approximate estimation is thus obtained of the extent to which the hæmoglobin of the blood of the mouse was saturated with carbon monoxide. From this the percentage of carbon monoxide in the air can be roughly estimated, since the blood of the mouse will be about two-thirds saturated with 0.16 per cent. of carbon monoxide in the air, half saturated with 0.08 per cent., a third saturated with 0.04 per cent., a fifth saturated with 0.02 per cent., etc. The tints should be compared by holding the test tubes against the light from the sky, and they should be changed from side to side during the comparison. The test requires daylight, but in its absence a lamp, or preferably an incandescent gas burner with a blue glass chimney and opal globe, may be used, or else blue glass spectacles.

If a mouse is not available, a sample of the air is collected in a bottle of 100 c.c. capacity, the cork removed under a dilute (about 0.5 per cent.) solution of blood, and about 5 c.c. of the solution allowed to enter the bottle; the cork is then replaced, the bottle covered with a cloth to protect it from light, which interferes with the reaction, and the contents shaken continuously for ten minutes. The solution is then poured into a test tube, and its content of carbon monoxide estimated as described above.

<sup>1</sup> Cf. *The Investigation of Mine Air*, by C. Foster and J. S. Haldane, p. 147.

The percentage of carbon monoxide ( $p$ ) may be calculated from the percentage saturation ( $s$ ) by the formula:—

$$p = \frac{s \times 0.07}{100 - s}$$

Thus, if the estimated saturation be 20 per cent., the percentage of carbon monoxide will be 0.017. A correction is necessary if the percentage of oxygen in the air examined is much below the normal, as the equilibrium attained between carbon monoxide and oxygen in blood depends upon the relative proportions of the two gases present in the air.

Haldane has also devised a less simple but more exact colorimetric test,<sup>1</sup> in which a standard solution of carmine is prepared so as to exactly match a 1 per cent. solution of blood saturated with carbon monoxide, when added in a certain proportion to a 1 per cent. solution of normal blood. The colorimetric comparison is made by adding the carmine solution from a burette to the diluted blood sample to be tested until its colour matches that of the above saturated solution.

**Colorimetric Test after the addition of Reagents.**—In this test, proposed by Kunkel and Welzel, the difference of colour of blood containing carbon monoxide and that free from carbon monoxide is observed after the addition of certain reagents which coagulate albumin.

The carbon monoxide is absorbed by 20 c.c. of a 20 per cent. solution of blood from a volume of air of about 10 litres, and the solution obtained, together with a control solution of normal blood, treated with the reagent. Various coloured precipitates are formed, which are of a reddish colour, but in the blood containing carbon monoxide the colour tends more towards a whitish blue, and in the normal blood solution more towards yellow or brown, if the quantity of carbon monoxide is small.

Welzel recommends the two following reagents:—(1) 15 c.c. of a 1 per cent. tannin solution are added to 5 c.c. of the blood solution and the whole shaken; the precipitate which results subsides gradually. A difference of colour occurs at once and becomes distinct after from one to two hours, and still more so after from twenty-four to forty-eight hours; the precipitate in the solution containing carbon monoxide is a brownish red, that in the normal blood solution a greyish brown. The difference in colour is still evident after nine months if the solutions are kept in well-closed vessels; (2) 5 c.c. of a 20 per cent. solution of potassium ferrocyanide and 1 c.c. of acetic acid (1 vol. glacial acetic acid + 2 vols. water) are added to 10 c.c. of the blood solution. The precipitate in the blood containing carbon monoxide soon becomes reddish brown, and that in ordinary blood, greyish brown. The difference in

<sup>1</sup> *Journal of Physiology*, 1897, 22, 478. Cf. Clowes and Redwood, *The Detection and Estimation of Inflammable Gas and Vapour in the Air*, p. 139.

colour decreases after half an hour, and disappears after from two to six days. Welzel detected 0.23 parts per 1000 of carbon monoxide in air by these two methods.

**The Flame Cap Test.**<sup>1</sup>—The cap produced above a hydrogen flame by combustible gases such as hydrocarbons, is also formed by carbon monoxide. Clowes has shown that with his standard hydrogen flame, a cap 12.5 mm. high is produced in air containing 0.25 per cent. of carbon monoxide, and that the cap increases in height proportionately with an increase in the percentage of carbon monoxide. As the same effect, however, is produced by other inflammable gases by which carbon monoxide is rarely unaccompanied, the test loses its specific value for the detection of this gas.

**The Quantitative determination of Carbon Monoxide.**—Apart from the analysis of the air of mines, exact quantitative estimations of carbon monoxide in air are seldom carried out. The ordinary methods of gas analysis can be employed for the estimation if the gas is present in sufficient quantity. (Cf. p. 210.) Haldane<sup>2</sup> has devised special apparatus for the analysis of mine air, both for laboratory use and for the analysis of the air *in situ*.

There are, in addition, a number of more special methods, of which the following are the most important:—For the determination of the comparatively large quantity of carbon monoxide present in tobacco smoke, Pontag<sup>3</sup> has worked out a method based on previous suggestions by Fodor. The sample is collected in a flask fitted with a double-bored cork, and a current of air, previously washed with a 0.2 per cent. solution of palladium chloride, passed through; the issuing air is passed first through a small flask containing fuming sulphuric acid to absorb hydrocarbons, then through sodium hydroxide solution for the removal of the sulphuric acid fumes, and finally through a series of four flasks containing a 0.2 per cent. solution of palladium chloride. The quantity of air passed through should be equivalent to at least five times the volume of the flask. The first flask is most strongly coloured by the liberated palladium, the second one faintly, the third scarcely perceptibly, and the fourth not at all. The metallic palladium is collected on a filter, washed with water, ignited, and weighed.

One mg. palladium = 0.263 mg. CO.

One c.c. CO weighs 1.2503 g. at 0° and 760 mm.

The iodometric method proposed by Fodor has been shown by Welischkowsky<sup>4</sup> to give good results. In this method the solution of palladium chloride, after having been acted upon by the carbon mon-

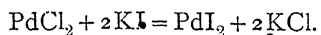
<sup>1</sup> Full details of these tests are given in *The Detection and Estimation of Inflammable Gas and Vapour in the Air*, by F. Clowes and B. Redwood, 1896.

<sup>2</sup> *The Investigation of Mine Air*, Foster and Haldane, pp. 100 and 115.

<sup>3</sup> *Z. Unters. Nahr. u. Genussm.*, 1903, 6, 673.

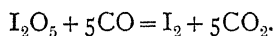
<sup>4</sup> *Arch. f. Hygiene*, 1, 227.

oxide in the air under examination, is filtered off from the precipitated palladium, heated to boiling, and potassium iodide solution (3.119 g. per litre, so that 1 c.c. = 1 mg. palladium) added, until no further precipitate of palladious iodide results on allowing to stand, boiling, and adding more palladious chloride drop by drop. The reaction takes place according to the equation:—



The method is very satisfactory when carefully carried out.

Spitta<sup>1</sup> has recently given a critical summary of the newer methods for the determination of small quantities of carbon monoxide, and has discussed especially the methods, published independently by Nicloux<sup>2</sup> and Gautier,<sup>3</sup> for the determination of carbon monoxide by iodine pentoxide. Both methods depend upon the reaction:—



Nicloux passes the gas under investigation through a U-tube which contains small pieces of potassium hydroxide, then over pumice soaked in sulphuric acid, and finally through a U-tube containing iodine pentoxide which is kept at a temperature of 150° in an oil-bath; an absorption tube containing 10 c.c. of sodium hydroxide is placed behind the tube of iodine pentoxide. The air is passed slowly through the tubes at a rate of, at most, 10 c.c. per minute; the iodine vapour set free is absorbed by the sodium hydroxide, then liberated by the addition of a few centigrammes of sodium nitrite and some sulphuric acid, and extracted with carbon disulphide or chloroform. The coloration obtained is compared with that given by a solution of potassium iodide containing 0.1 mg. per c.c., when treated with nitrite and sulphuric acid and extracted with chloroform, varying quantities of which are treated until the coloration obtained in the test is matched. One hundred and twenty-seven parts by weight of iodine correspond to 70 parts by weight of carbon monoxide, or 1 c.c. of *N*/100 iodine solution = 0.7 mg. carbon monoxide.

According to Kinnicutt and Sanford,<sup>4</sup> better results are obtained by titrating the liberated iodine directly with *N*/100 sodium thiosulphate.

In Gautier's method the iodine is not determined, but the carbon dioxide formed is estimated after liberation from the resulting carbonate with acids. The method, which, of course, presupposes that the exact amount of carbonate present in the potassium hydroxide is known, is somewhat more complicated than that of Nicloux. The chief objection to the method is that, according to Gautier, although iodine pentoxide is not acted upon by hydrogen, methane, or by aromatic hydrocarbons,

<sup>1</sup> *Arch. f. Hygiene*, 46, 284; *J. Soc. Chem. Ind.*, 1903, 22, 652.

<sup>2</sup> *Comptes rend.*, 1898, 126, 746.

<sup>3</sup> *Ibid.*, 1898, 126, 931.

<sup>4</sup> *J. Amer. Chem. Soc.*, 1900, 22, 14.

it is partially reduced both by ethylene and by acetylene. The errors thus introduced in presence of these gases can be overcome, but the methods involved are complicated and lengthy. Levey and Pécoul state, however, that the action of acetylene can be neglected in most cases, as 1 part per 10,000 has no reducing effect, whereas 1 part per 10,000 of carbon monoxide gives an intense coloration. A further important disadvantage, emphasised by Spitta, is the very small quantity of air which can be used for the determination, as at most not more than from 600 to 1500 c.c. per hour can be passed through the apparatus. The combustion of carbon monoxide by palladium asbestos by Winkler's method is also unsatisfactory; the combustion is incomplete unless the experiment be carried out extremely slowly. The method is therefore only applicable for small quantities of air containing a considerable percentage of carbon monoxide.

A more recent method devised by Spitta<sup>2</sup> consists in oxidising the carbon monoxide in a large quantity of air by means of heated electrodes made of silver foil coated with palladium. It is stated that exact determinations of carbon monoxide to within 0.1 part per 1000 can be thus obtained. The temperature of the palladium must be maintained at 150° to 160°; at higher temperatures (180° to 200°) ethane, ether, petroleum vapour, and benzene are oxidised, and above 250° acetylene; ethylene is not oxidised below 300°. The combustion of the carbon monoxide requires about one and a half hour, and to obtain good results a small proportion of hydrogen must be present. The carbon dioxide formed is afterwards determined by Pettenkofer's method. A parallel determination of the carbon dioxide in a corresponding volume of the air is carried out; the quantity of carbon dioxide which has resulted from the carbon monoxide is then obtained by difference.

##### 5. Hydrocarbons: Methane, Acetylene, Benzene, Petroleum Vapour.

Attempts have frequently been made to estimate small quantities of compounds containing much carbon, such as the above, by passing a large volume of the air (from 5 to 10 litres) first through concentrated potassium hydroxide solution to remove carbon dioxide, then through baryta water to show that the absorption has been complete, and finally through a combustion tube containing red-hot copper oxide, which combusts all gaseous carbon compounds to carbon dioxide and water; the carbon dioxide formed is absorbed by baryta water and determined by titration. It is, of course, frequently a matter of difficulty to calculate the carbon dioxide to any definite compound, since the nature of the organic impurities in air are often indefinite.

° Spitta's method for the estimation of carbon monoxide by oxidation by heated palladium (p. 896) can also be used for hydrocarbons; in this

<sup>1</sup> *Comptes rend.*, 1906, 142, 162.

<sup>2</sup> *Loc. cit.*

case, however, a higher temperature must be used than for carbon monoxide.

The estimation of *Methane* is of the greatest importance in the examination of the air of mines, especially as a check on efficient ventilation, in association with the estimation of the carbon dioxide. Apart from the ordinary methods of analysis that can be used for its determination, for which Haldane's portable apparatus<sup>1</sup> is especially suitable for testing the air of mines, Le Chatelier's<sup>2</sup> limit of inflammability test, in which measured proportions of methane are added successively to the gas under examination until the limit of inflammability with air (6.1 per cent.) is reached, is very applicable and reliable; the "Flame-cap" test<sup>3</sup> is also important as a direct indication of the proportion of fire-damp in mine air. The combustion of methane by a heated platinum spiral (*cf.* p. 203) gives reliable results; a simplified form of apparatus for its determination in mine air by this method has been devised by Brunck.<sup>4</sup>

Very few special methods are known for the identification of hydrocarbons in small quantities.

The following qualitative reaction for *Acetylene* has been described by L. Ilosvay.<sup>5</sup> One g. of crystallised copper sulphate is dissolved in a little water, 4 c.c. of a 20 per cent. ammonia solution and 3 g. of hydroxylamine hydrochloride added, and the whole diluted to 50 c.c.; the cuprous solution thus prepared keeps for a few days. For the detection of acetylene, a plug of cotton wool or glass wool is soaked with the reagent and the gas to be tested passed over the plug, or the gas is shaken with a few c.c. of the reagent; in either case the presence of acetylene is indicated by a red coloration or precipitate.

Acetylene may be estimated quantitatively by passing the gas through an ammoniacal silver solution; the precipitated silver acetylide ( $C_2H_2Ag_2O$ ) is filtered off, decomposed, and weighed as silver chloride. The acetylene may also be absorbed in an ammoniacal solution of cuprous chloride, the precipitate ( $C_2H_2Cu_2O$ ) filtered off, washed with dilute ammonia until the filtrate is free from copper, the copper acetylide dissolved in hydrochloric acid, and the contained copper estimated either electrolytically, or iodometrically, or, if its quantity is very small, colorimetrically. Carbon monoxide is, of course, also absorbed by cuprous chloride, but gives no precipitate; any carbon dioxide or hydrogen sulphide in the gas tested must be removed by washing with sodium hydroxide, previous to the absorption of the acetylene.

4.89 mg. Cu = 1 mg. Acetylene,

8.3 mg. Ag = 1 mg. Acetylene.

<sup>1</sup> *The Investigation of Mine Air*, p. 115.

<sup>2</sup> *Ibid.*, p. 76.

<sup>3</sup> *Cf.* Clowes and Redwood, *The Detection and Estimation of Inflammable Gas and Vapour in the Air*, p. 54 *et seq.*

<sup>4</sup> *Cf.* *The Investigation of Mine Air*, p. 51.

<sup>5</sup> *Ber.*, 1899, 32, 2697.



*Benzene* may be detected qualitatively, and, if present in sufficient quantity, may be determined quantitatively by the method of Harbeck and Lunge,<sup>1</sup> in which the air is slowly passed through a tube with fifteen bulbs, filled with a mixture of equal parts by weight of concentrated sulphuric acid and fuming nitric acid. The benzene is converted into dinitrobenzene, which may be detected by its smell, and can be extracted from the liquid, after neutralisation with ether. (Cf. "Illuminating Gas," Vol. II.)

*Petroleum vapour* in air can be detected and estimated by the Clowes' flame-cap test, and also by a manometric method suggested by Dewar and worked out by Redwood.<sup>2</sup>

## 6. Organic Matter.

It has been suggested<sup>3</sup> to estimate organic matter in the air, as in water, by its reducing action upon an acid solution of potassium permanganate. Such a method is open to the objection that the action of the various gases on permanganate is entirely unknown, but by adhering to strictly uniform conditions, comparative values may be obtained which may be of use in special cases.

As the completeness of the oxidation of organic matter by permanganate depends upon the intimacy of the contact of the air with the solution, the length of time during which the action proceeds, and the temperature, the conditions must be arranged so that the air passes through the potassium permanganate in as fine a stream as possible and remains as long as possible in contact with it. These conditions are fulfilled by the wash-bottles devised by Archarow<sup>4</sup> in which the column of permanganate solution is about 13 cm. high, when 10 c.c. of the liquid are introduced, and in which the air is broken up into small bubbles by a tube drawn out to a fine point, which dips nearly to the bottom of the vessel. For the estimation, the air is passed successively through three of these wash-bottles, which are kept at a temperature of from 40° to 45° in a water-bath, to facilitate the oxidation; the dust in the air is prevented from coming into contact with the permanganate by a plug of glass wool, previously boiled with dilute permanganate and washed with water, which is placed in a tapering tube attached by means of a ground-glass joint to the inlet tube of the first wash-bottle.

The solutions required are: (1) a solution of oxalic acid containing 0.7879 g. of recrystallised and dried oxalic acid in 1 litre of water, so that 10 c.c. of the solution require 1 mg. of oxygen for its oxidation

<sup>1</sup> *Z. anorg. Chem.*, 1898, 16, 26.

<sup>2</sup> For details of these tests, cf. *The Detection and Estimation of Inflammable Gases and Vapour in the Air*, loc. cit., pp. 168-197.

<sup>3</sup> Cf. Hefelmann, *Arch. f. Hygiene*, 8, 262.

<sup>4</sup> *Arch. f. Hygiene*, 13, 229.

(*cf.* "Drinking Water and Water Supplies," p. 742); (2) a solution of potassium permanganate containing 0.395 g. of the crystallised salt in 500 c.c. of water. For the determinations, 5 c.c. of each of the solutions are diluted to 250 c.c. so as to reduce the error of the titrations as much as possible. The permanganate solution is acidified with 2.5 c.c. of dilute sulphuric acid (1 : 3), boiled, and after cooling poured into the wash-bottles; it must be standardised before each determination.

At the conclusion of the experiment the potassium permanganate solution is poured into a porcelain dish, 10 c.c. (one-third of the whole) transferred to a flask, and heated to boiling after the addition of 3 drops of sulphuric acid (1 : 3); the quantity of oxalic acid which originally corresponded to 10 c.c. of permanganate is then added, the solution again boiled for *exactly* two minutes, and then quickly titrated with permanganate, until a perceptible red coloration is obtained. The titration of the control solution is carried out similarly. For the calculation, the quantity of potassium permanganate used in the control experiment is deducted from the quantity required in the actual estimation; the result is expressed in terms of the oxygen required for the oxidation of the organic matter. (*Cf.* p. 742.)

According to Erismann and Archarow, the difference in the quantity of organic matter in different places can be shown by this method if the variation amounts to at least 25 per cent.

The Manchester Air Analysis Committee (*loc. cit.*) determined the organic matter in air by aspirating the sample through a plug of cleaned glass wool placed in a tube 20 cm. long and 12 mm. in diameter. After a sufficient quantity of air had been drawn through, the plug was transferred to a stoppered cylinder containing 100 c.c. of potassium permanganate solution (0.395 g. per litre) and an equal volume of dilute sulphuric acid (1 : 3); after stirring up the glass wool with the solution the unchanged permanganate was titrated in successive portions of 10 c.c. each, at once, after one hour, six hours, twenty-four hours, and after digesting for one hour at 50° respectively. The results are, as in the above method, only comparative, and include any organic matter present as dust.

Should it be desired to determine the nitrogen in the organic matter (albuminoid ammonia), the solutions obtained in either of the above methods can be distilled with alkaline permanganate, and the liberated ammonia estimated. (*Cf.* p. 769.)

### 7. Soot and Smoke.

No direct quantitative methods have been used for the estimation of soot in ordinary air. Obviously it would be necessary to aspirate very large quantities of air through a filter of inorganic material, such as glass wool, and then to determine the carbon by combustion. Several

methods have, however, been employed for judging the relative quantity of soot in air.

L. Heim<sup>1</sup> exposed dishes of water to the air, collected the soot obtained on filter paper, taking care not to include grains of sand or insects which might have fallen into the water, and determined the increase in weight; the method can be checked to some extent by observing the degree of blackening of the filter paper. The method is liable to a number of drawbacks which are difficult to eliminate, and might be improved by collecting the soot on asbestos filters and determining the contained carbon.<sup>2</sup>

The soot (blacks) collected by snow has been made use of by the Manchester Air Analysis Committee as a comparative means of testing the purity of the air in winter. Also, the deposits of soot formed on the roofs of greenhouses have been analysed, with the view of determining their approximate composition and character. The deposits thus collected at Chelsea and at Kew during very foggy weather in February 1901, gave the following analytical results:<sup>3</sup>—

	Chelsea. Per cent.	Kew. Per cent.
Carbon . . . . .	39	42.5
Hydrocarbons . . . . .	12.3	} 4.78
Organic bases . . . . .	2.0	
Sulphuric acid . . . . .	4.33	4.0
Hydrochloric acid . . . . .	1.43	0.83
Ammonia . . . . .	1.37	1.14
Metallic iron and magnetic oxide . . . . .	2.63	} 41.15
Other mineral matter, chiefly silica and ferric oxide . . . . .	31.24	
Water not determined.		

More recent determinations of the constituents of Manchester soot by Knecht<sup>4</sup> gave 10.7 per cent. of ammonium sulphate, 19.6 of mineral matter (ash), 10.9 soluble in dilute sulphuric acid, 13.0 soluble in benzene, and 45.8 per cent. of carbon by difference. London soot contained considerably less extractive matter.

For the determination of soot in the chimneys of factories, P. Fritzsche recommends the following as a simple method:—A tube 150 mm. long and 10 mm. in diameter, is plugged with 2 g. of loose cellulose (as used for preparing nitrocellulose), and attached at one end to a connecting tube which passes through a hole into the chimney, the other end being connected with an aspirator, by means of which from 10 to 20 litres of the chimney gases are aspirated through the tube. Most of the soot is collected at the beginning of the plug. This blackened portion is introduced into a wide-necked,

<sup>1</sup> *Arch. f. Hygiene*, 26.

<sup>2</sup> Cf. Mabery, *J. Amer. Chem. Soc.*, 1895, 17, 105.

<sup>3</sup> F. W. Oliver, *J. Royal Horticultural Society*, 1893, 16, 1.

<sup>4</sup> *Mem. and Proc., Manchester Lit. and Phil. Soc.*, 1905, 49 [14].

stoppered flask of 300 c.c. capacity, and the rest used to clean out the tube and also placed in the flask, together with 200 c.c. of water. The whole is then shaken to a grey suspension, which is filled into a large test tube from 40 to 50 mm. in diameter. Similar tubes are filled with 2 g. of cellulose, 200 c.c. of water, and known quantities of soot (from 15 to 30 mg.), and well shaken, which are used for a colorimetric comparison; a permanent scale can be prepared from these standards with black paper.<sup>1</sup>

A method devised by Rubner<sup>2</sup> has given interesting comparative results, but has hitherto been used more as a qualitative than as a quantitative method. From 2000 to 4000 litres of the air to be examined are drawn through circular pieces of filter paper of 2 cm. diameter stretched in a metal frame. The coloration produced is approximately proportional to the quantity of soot present in the air. Even air which has passed through a plug of cotton wool gives a trace of discoloration on the paper. Petroleum lamps, Argand burners, and stearin candles give easily detectable quantities of soot as compared with the incandescent burner.

A similar method has been used for many years in gasworks for the approximate estimation of the coal tar remaining in the gas after purification.

### 8. Dust.

Air, in the open, contains usually so little dust that a quantitative estimation is a matter of difficulty, and is but rarely carried out. Quantities of 1 mg. per cb.m. are considered high in the open air, and in general no weighable quantity is obtainable from 100 to 200 litres.

For this reason, Lehmann and Arens<sup>3</sup> have worked out a comparative method for estimating the quantity of dust in air. Beakers of 400 sq. cm. superficial area are inverted on a piece of wood, fixed on a rod about 5 feet from the ground, and are covered with a thin layer of grease, so that all dust particles which come in contact with it remain attached. After being exposed for certain periods such as a quarter of an hour, one hour, or three hours, according to the amount of dust and the prevailing air currents, the grease is dissolved in ether, and filtered through a weighed filter paper; the filter paper is then extracted with ether and the increase of weight, due to the residual dust, determined. By this method, a distinct increase of weight can be obtained in cases in which the examination of several hundred litres of air gives no perceptible quantity of dust.

For the determination of larger quantities of dust, such as occur in closed spaces, measured quantities of air are filtered through small

<sup>1</sup> *Z. anal. Chem.*, 1898, 37, 92.

<sup>2</sup> *Hygien. Rundschau*, 1900, 257.

<sup>3</sup> *Arch. f. Hygiene*, 21.

light glass tubes, from 1 to 1.5 cm. in diameter, closed at one end with a plug and drawn out to a fine point at the other. The difference in the weight of the well-dried tube with its plug, before and after the experiment, gives the amount of dust, which is generally calculated to the quantity per cubic metre. It is most convenient to aspirate the air with an air-pump, and to measure the quantity passed through with a gas-meter. If no other means are at hand, a useful method is to aspirate the air with a gas-tight bellows of about 20 litres capacity, fitted with a three-way tap; 20 litres of air are first aspirated into the bellows through the plugged tube, the tap is then reversed, the filtered air blown into the open air, and the operation repeated until from 200 to 400 litres of air have been aspirated through the tube. At least 100 litres should be used for a determination.

The determination of the coal dust in the air of coal mines, which apart from hygienic considerations has become of considerable importance on account of the part it plays in colliery explosions, is effected by drawing a measured volume of the air through a tube about 16 cm. long and 15 mm. in diameter, which is drawn out below to a narrow piece 3 cm. long, and is widened out a little at the top; the tube is filled with a packing of cotton wool of a length of about 10 cm., and is provided with glass caps for the two ends. The tube, together with the caps, is weighed before and after the experiment, and the increase of weight calculated per cubic metre of air; 10 litres of air is a suitable quantity for the estimation.<sup>1</sup>

For the estimation of stone dust in metalliferous mines, Haldane<sup>2</sup> uses a tube about 8 cm. long and 12 mm. in diameter, drawn out at one end, and fitted with a small plug of cotton wool. The tube is attached to the nozzle of a brass exhausting syringe of about 200 c.c. capacity, for the determination and the air under examination drawn through, the syringe and tube being held in a horizontal position. The plug is subsequently transferred to a platinum crucible and ignited; the weight of the ash of the cotton wool can be neglected.

Should an analytical examination of the dust be desired, the usual methods can, as a rule, be employed, provided the quantity of dust collected is sufficient. If the contained carbon is to be estimated, the dust can be collected on a glass wool filter, and subsequently combusted. The microscopic examination of dust has been studied by Wegmann.<sup>3</sup>

The following table gives some indication as to the quantity of

<sup>1</sup> Cf. Foster and Haldane, *The Investigation of Mine Air*, p. 57.

<sup>2</sup> *Ibid.*, p. 120. Also, *Report on the Health of Cornish Miners*, by Haldane, Martin and Thomas. Blue Book [Cd. 2091], 1904. Published by Eyre & Spottiswoode.

<sup>3</sup> *Arch. f. Hygiene*, 21.

dust in the air of rooms and workshops as determined by Hesse<sup>1</sup> and by C. Arens;<sup>2</sup> the data are expressed in mg. per cubic metre.

Study . . . . .	0
Living room . . . . .	1.6
Laboratory . . . . .	1.4
Stoneworkers' workshop (half in the open air) . . . . .	8.7
Artificial wool factory (combing-room) . . . . .	7.0
" " (cutting-room) . . . . .	20.0
Saw-mill . . . . .	15-17.0
Mills . . . . .	4.4, 22, 28, 47
Iron foundry.—Experiment I. Commencement of work . . . . .	1.5
Experiment II. Few workmen present . . . . .	12.0
Experiment III. Cleaning-room . . . . .	71.7
Snuff factory . . . . .	16.72
Felt shoe factory . . . . .	175
Cement works (a) during work . . . . .	224
(b) during interval . . . . .	130

### III.—THE ESTIMATION IN AIR, OF THE IMPURITIES ASSOCIATED WITH SPECIFIC INDUSTRIES

The impurities included in this division arise in most cases from specific manufacturing operations, and may occur in the air of the works concerned or in that of their more immediate surroundings.

#### 1. Chlorine, Bromine, and Iodine.

As large a quantity of air as possible is passed through 15 to 20 c.c. of a freshly prepared, colourless solution of potassium iodide, and then through a vessel containing  $N/10$  sodium thiosulphate solution. In presence of chlorine or bromine, the potassium iodide solution is coloured brown by the liberated iodine. The solution is washed into a beaker and the iodine titrated with  $N/10$  or  $N/100$  sodium thiosulphate; 1 c.c.  $N/10$  sodium thiosulphate corresponds to 7.996 mg. of bromine and to 3.545 mg. of chlorine. The quantity of iodine vapour which has been carried over from the potassium iodide solution to the sodium thiosulphate receiver is determined by titrating with  $N/100$  iodine solution and is added to the amount found by direct titration.

Iodine is similarly estimated by absorption with a solution of potassium iodide; 1 c.c.  $N/10$  sodium thiosulphate = 12.697 mg. of iodine.

#### 2. Phosphorous Trichloride.

Phosphorous trichloride is converted quantitatively into phosphorous and hydrochloric acids in presence of water. The air to be examined is passed through a solution of sodium hydroxide and the hydrochloric acid determined.<sup>3</sup>

<sup>1</sup> *Dingl. polyt. J.*, 1881, 240, 52.

<sup>2</sup> *Arch. f. Hygiene*, 21.

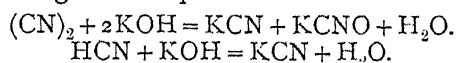
### 3. Hydrofluoric Acid.

According to Fellner,<sup>1</sup> hydrofluoric acid, if present in considerable quantities, can be absorbed in potassium hydroxide solution and titrated with phenolphthalein as indicator after boiling; any hydrofluosilicic acid formed behaves similarly to hydrofluoric acid in the titration. If the solution is not boiled, the results are too low.

The quantitative determination of minute traces of hydrofluoric acid, such as occur in the vicinity of aluminium works in which aluminium fluoride is used, is a matter of extreme difficulty.<sup>2</sup>

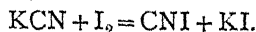
### 4. Cyanogen and Hydrocyanic Acid.

Potassium hydroxide absorbs both hydrocyanic acid and cyanogen from the air, according to the equations:—



Hydrocyanic acid is very seldom found in the air in quantities sufficient for titration. The absorption by alkali hydroxide takes place quantitatively. The estimation of the absorbed gas is effected either by titration with silver nitrate or iodometrically. In the former method the liquid is faintly acidified with sulphuric acid, as much chalk as will cover the point of a knife added together with a few drops of potassium chromate, and then titrated with silver nitrate solution until a brownish coloration appears. One c.c. *N*/10 silver nitrate = 2.702 mg. HCN.

In the iodometric determination the alkaline solution is neutralised by the addition of sulphuric acid and chalk, and titrated with iodine in presence of starch; 1 c.c. *N*/100 iodine solution = 1.35 mg. HCN.



If, as is generally the case, cyanogen has to be determined in absence of hydrocyanic acid, the estimation is similarly carried out; 1 c.c. *N*/10 silver nitrate solution = 5.2 mg. (CN)<sub>2</sub>.

### 5. Hydrogen Phosphide (PH<sub>3</sub>).

Only traces of this extremely poisonous gas occur in the air of laboratories and of works. The best method for the estimation of such minute quantities is to pass a large volume of the air either through nitric acid or through bromine water, and to determine the phosphoric acid formed in the usual way;<sup>3</sup> 1 mg. P<sub>2</sub>O<sub>5</sub> = 0.48 mg. PH<sub>3</sub>. Volumetric methods are not applicable.

### 6. Hydrogen Arsenide.

This gas is readily detected in the air by its garlic-like odour, even when present in such minute quantities that it can scarcely be deter-

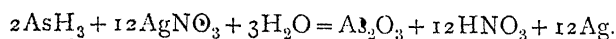
<sup>1</sup> *Chem. Zeit.*, 1895, 29, 1143.

<sup>2</sup> Cf. Wislicenus, *Z. angew. Chem.*, 1901, 14, 705.

<sup>3</sup> Cf. Yokote, *Arch. f. Hygiene*, 49.

mined quantitatively; it can also be detected by passing the air through a solution of silver nitrate (if hydrogen sulphide and hydrogen phosphide are known to be absent) by the darkening of the solution.

For the quantitative estimation, the air is passed through a series of wash-bottles containing silver nitrate solution, the excess of silver nitrate precipitated as chloride with hydrochloric acid, and the arsenic determined in the filtrate as  $\text{Mg}_3\text{As}_2\text{O}_7$ .



### 7. Mercury Vapour.

Mercury vapour may be detected qualitatively in the air by exposing strips of gold leaf in suitable places, and observing whether any grey coloration is formed. A better method is that due to Kunkel, in which the dry air is passed through a tube from 2 to 3 mm. wide and 25 cm. long, and slightly bent in the middle, containing a few particles of iodine; a deposit of red or reddish-yellow mercuric iodide is formed just beyond the iodine if any mercury vapour is present in the air, and the quantity may be approximately gauged. The air should not pass through the tube at a greater rate than 1 litre in from eight to ten minutes.

For the quantitative determination, a useful method is to absorb the mercury vapour in weighed tubes or flasks containing gold leaf.<sup>1</sup>

Kunkel has also shown that his qualitative test can be used for the quantitative estimation of mercury vapour. The deposited mercuric iodide is dissolved in potassium iodide, filtered from any particles of solid iodine present, and sufficient sodium hydroxide added to the filtrate to combine with any free iodine. The mercury is then determined colorimetrically as the black sulphide by adding ammonium sulphide to the solution, and comparing the coloration with that imparted to faintly alkaline solutions of mercuric chloride on similar treatment; or the mercury may be deposited by electrolysis and weighed.<sup>2</sup> The maximum quantity of mercury vapour which can be present in 1 cb.m. of air at 0° is approximately 2 mg.; at 10°, 6 mg.; at 20°, 14 mg.; and at 30°, 31 mg.

### 8. Carbon Bisulphide.

This can generally be detected qualitatively by its characteristic smell. For the quantitative determination, Lehmann<sup>3</sup> recommends the method due to Gastine, in which the carbon bisulphide is absorbed

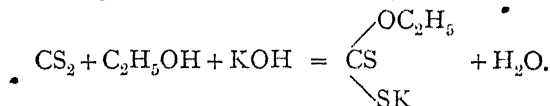
<sup>1</sup> Cf. Hilger and Raumer, *Forschungsberichte über Lebensmittel*, 1, 32; also, Renk, *Arch. d. Gesundheitsamts*, 5, 113.

<sup>2</sup> Cf. Kunkel and Fessel, *Verhandl. der phys.-med. Gesellsch., Würzburg*, 32, 1.

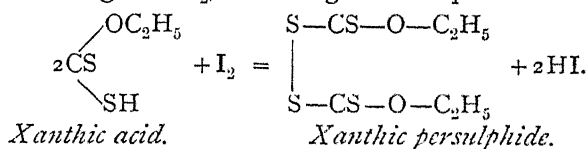
<sup>3</sup> K. B. Lehmann, *Arch. f. Hygiene*, 20.



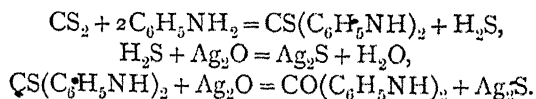
by a concentrated solution of potassium hydroxide in 96 per cent. alcohol, when it is completely converted into potassium xanthate.



For the estimation, the contents of the absorption flask are washed out with a mixture of equal parts of alcohol and water, slightly acidified with acetic acid, and neutralised with calcium carbonate. A solution of starch is then added, together with a quantity of water about equal to that of the alcoholic potassium hydroxide originally employed, and the liquid titrated with a solution of iodine containing 1.668 g. per litre until a faint blue coloration is obtained. One c.c. of iodine solution corresponds to 1 mg. of  $\text{CS}_2$ , according to the equation:—



Schmitz-Dumont<sup>1</sup> passes the carbon bisulphide vapour through a mixture of 50 c.c. of 5 per cent. silver nitrate solution and 5 c.c. of aniline, which is kept at a temperature of 60°. The following reactions take place:—



The silver sulphide thus formed is filtered off, fused with sodium carbonate and nitre, and the resulting sulphuric acid determined as barium sulphate.

### 9. Ether Vapour.

Ether vapour may be absorbed quantitatively from an enclosed volume of air by sulphuric acid of sp. gr. 1.84 in about thirty minutes, and may thus be determined volumetrically.<sup>2</sup>

At 10° the vapour tension of ether is 286 mm.; saturated air contains 38.1 per cent. by volume.

At 20° the vapour tension of ether is 435 mm.; saturated air contains 58 per cent. by volume.

At 30° the vapour tension of ether is 637 mm.; saturated air contains 84.9 per cent. by volume.

### 10. Mercaptan.

Rubner has proposed several reactions for the detection of this intensely disagreeable smelling gas, which occurs in small quantities in

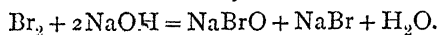
<sup>1</sup> *Chem. Zeit.*, 1897, 21, 487, 510.

<sup>2</sup> Cf. Horwitz, *Medical Dissert.*, Würzburg, 1900.

animal exhalations, on boiling vegetables, and in the air of some drains. As a qualitative test he recommends the grass-green coloration imparted to porous earthenware soaked with a solution of isatin in sulphuric acid; the air should be dried over calcium chloride, and then passed through tubes containing the pieces of earthenware. First a green and then a bluish-green colour is obtained. A quantitative determination in air is scarcely practicable; when lead nitrate is used as an absorbent, quantitative results are only obtained if very precise conditions are observed in regard to the concentrations of the solution employed.<sup>1</sup>

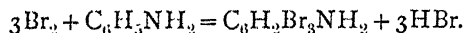
## II. Aniline.

No method has hitherto been worked out for the determination of aniline in air. According to experiments by Lehmann, however, good results may be obtained as follows:—The aniline is absorbed by passing the air through two absorption vessels connected in series, containing 10 per cent. sulphuric acid (not hydrochloric); the bulk of the acid is then neutralised, and the solution titrated with bromine solution, the strength of which has been previously determined with potassium iodide and sodium thiosulphate. The bromine solution is prepared by dissolving 3 to 4 g. of bromine in 1 litre of water, and adding sodium hydroxide until the colour of the solution is changed from brown to yellow. The action of the sodium hydroxide is as follows:—



On addition of acid, the whole of the bromine is again liberated. This solution has the advantage of keeping better than bromine water.

The bromine reacts with the aniline to form tribromoaniline, according to the equation:—



Lehmann has carefully tested this reaction, with the object of applying it as a volumetric method. According to the equation, 1 c.c. of *N*/10 bromine solution =  $\frac{9.3}{6} = 1.55$  mg. aniline.

*Example*:—10 c.c. of bromine solution were acidified, treated with potassium iodide, and titrated with *N*/10 sodium thiosulphate; the quantity required was 5.95 c.c.; hence the 10 c.c. contained 5.95 c.c. of *N*/10 bromine solution. The sulphuric acid in the two absorption vessels was nearly neutralised and then made up to 250 c.c.; 25 c.c. required 15.7 c.c. of bromine solution, therefore 250 c.c. corresponded to 157 c.c. of bromine solution =  $\frac{157 \times 5.95 \times 1.55}{10}$  mg. of aniline. Hence the air contained 145 mg. of aniline. By direct weighing of the flask from

<sup>1</sup> Cf. Rubner, *Arch. f. Hygiene*, 19, 156.

which the aniline had been obtained by passing a current of dry air, the loss of aniline was found to be 144 mg. The method is also applicable to the determination of very much smaller quantities of aniline.

### EFFECTS OF THE IMPURITIES IN AIR

The gaseous impurities present in air may produce injurious effects upon man either on account of the diminution they cause in the percentage of oxygen present, or because of their direct poisonous action; similarly they may cause direct injury to vegetation. The chief impurities in these respects are the following:—Excess of carbon dioxide, deficiency of oxygen, sulphur dioxide, hydrogen sulphide, carbon monoxide, and dust.

The table on page 909, prepared by Lehmann, gives a summary of his own investigations, together with those of his pupils, on the injurious effects of impurities that may be present in air. The data were obtained by experiments on cats; those given in columns 2 and 3 were confirmed, in a number of instances, by experiments on man.

The concentrations given in column 4 would probably be harmless even on prolonged inhalation, in most cases. This has been proved for many of the gases, but requires further investigation in other cases. According to Lehmann, man gradually becomes capable of withstanding from three to four times as much sulphur dioxide as at first, without harmful effects;<sup>1</sup> this holds also for ammonia and for chlorine in the case of animals, but not for hydrogen sulphide.<sup>2</sup>

The injurious effects of impurities in air have also been very thoroughly studied by Haldane, especially in relation to the air of collieries and mines, and to poisoning by carbon monoxide. The results of his experiments are given in *The Investigation of Mine Air*, by Foster and Haldane, pp. 142-56, and are also embodied in the following Government Reports; the data include suggestions as to the permissible limits that should be assigned to the more important of the impurities dealt with:—

*Causes of Death in Colliery Explosions and Underground Fires.* [C. 8112], 1896.

*The Composition of the Air in the Metropolitan and other Railway Tunnels*, 1897.

*Manufacture and use of Water Gas, and other Gases containing a large proportion of Carbonic Oxide.* Report of the Departmental Committee [C. 9164], 1899.

*Ventilation of Factories and Workshops.* First Report of the Departmental Committee [Cd. 1302], 1903; Second Report [Cd. 3553], 1907; Part II., Appendix [Cd. 3553], 1908.

<sup>1</sup> *Arch. f. Hygiene*, 18.

<sup>2</sup> *Arch. f. Hygiene*, 34.

The results are given in some cases in volumes per thousand, and in others in milligrams per litre.	Quantity causing rapid death. 1.	Concentration which in $\frac{1}{2}$ to 1 hour causes illness and danger to life. 2.	Concentration which produces no serious effect in $\frac{1}{2}$ to 1 hour. 3.	Concentration which gives only slight symptoms after several hours. 4.	Author and Reference.
Hydrochloric acid gas	...	1.5-2 $\frac{g}{100}$	0.05 or at most 0.1 $\frac{g}{100}$	0.01 $\frac{g}{100}$	K. B. Lehmann, <i>Arch. f. Hygiene</i> , 5; Matt, <i>Diss. Würzburg</i> , 1889.
Sulphurous acid	...	0.4-0.5 $\frac{g}{100}$	0.05 $\frac{g}{100}$	0.02-0.03 $\frac{g}{100}$	Ogata, <i>Arch. f. Hygiene</i> ; K. B. Lehmann, <i>Arch. f. Hygiene</i> , 19.
Hydrocyanic acid	about 0.3 $\frac{g}{100}$	0.12-0.15 $\frac{g}{100}$	0.05-0.06 $\frac{g}{100}$	0.02-0.04 $\frac{g}{100}$	K. B. Lehmann and Wagschal ( <i>Dissertation</i> ).
Carbon dioxide	30 $\frac{g}{100}$	about 60-80 $\frac{g}{100}$	40-60 $\frac{g}{100}$	20-30 $\frac{g}{100}$	Emmerich, Friedländer, and Herler, <i>Z. physiol. Chem.</i> , 2.
Ammonia	...	2.5-4.5 $\frac{g}{100}$	0.3 $\frac{g}{100}$	0.1 $\frac{g}{100}$	K. B. Lehmann, <i>Arch. f. Hygiene</i> , 5, 34.
Chlorine and bromine	about 1 $\frac{g}{100}$	0.04-0.06 $\frac{g}{100}$	0.003 $\frac{g}{100}$	0.001 $\frac{g}{100}$	K. B. Lehmann, <i>Arch. f. Hygiene</i> , 7; Matt, <i>loc. cit.</i>
Iodine	3.5 mg.	0.3-0.5 mg.	0.003 $\frac{g}{100}$	0.0005-0.001 $\frac{g}{100}$	Matt, <i>loc. cit.</i>
Phosphorus trichloride	...	0.4-0.6 $\frac{g}{100}$	0.01-0.02 mg.	0.004 mg.*	K. B. Lehmann and Butjagin, <i>Arch. f. Hygiene</i> , 14.
Hydrogen phosphide	...	0.3-0.5 mg.	0.1-0.2 $\frac{g}{100}$	...	K. B. Lehmann and Yokote, <i>Arch. f. Hygiene</i> , 14.
Hydrogen sulphide	1-2 $\frac{g}{100}$	0.5-0.7 $\frac{g}{100}$	0.2-0.3 $\frac{g}{100}$	0.1-0.15 $\frac{g}{100}$	K. B. Lehmann, <i>Arch. f. Hygiene</i> , 14.
Petroleum vapour	...	...	15-25 mg.	5-10 mg.	.....
Benzene	...	...	10-15 mg.	about 5 mg.	.....
Carbon bisulphide	...	10-12 mg.	2-3 mg.	1-1.2 mg.	.....
Carbon tetrachloride	300-400	about 150-200 mg.	about 25-40 mg. per litre	about 10 mg.	K. B. Lehmann, <i>Arch. f. Hygiene</i> , 14.
Chloroform	300-400	70	25-30 mg.	about 10 mg.	K. B. Lehmann and Behr ( <i>Dissertation</i> ).
Carbon monoxide	...	2.3 $\frac{g}{100}$	0.5-1.0 $\frac{g}{100}$	0.2 $\frac{g}{100}$	Max Gruber, <i>Arch. f. Hygiene</i> , 2.
Aniline and toluidine	...	...	0.4-0.6 mg.†	0.1-0.25 mg.	K. B. Lehmann and Flögel ( <i>Dissertation</i> ).
Nitrobenzene	...	...	1.0 mg.‡	0.2-0.4 mg.	K. B. Lehmann and Zieger ( <i>Dissertation</i> ).

\* Even as small a quantity as 0.025  $\frac{g}{100}$  taken for about six hours per day sufficed to produce certain death.

† Quantities over 0.8 mg. per litre generally kill cats, if taken for more than five hours.

‡ The maximum quantity of nitrobenzene which can be brought into the air is about 1 mg. per litre; it never acts as a powerful poison when inhaled.

<sup>a</sup> *The Health of Cornish Miners.* Haldane, Martin, and Thomas [Cd. 2091], 1904.

*The Use of Water Gas and other Gases in Factories.* Home Office Memorandum, 1906.

The effect of air impurities, especially in association with fog, upon cultivated plants has been investigated by Oliver,<sup>1</sup> and H. Wislicenus<sup>2</sup> has studied the injurious action of a number of impurities upon vegetation.

According to the latter author, acids, etc., act harmfully in the following order, the last mentioned being the most injurious:  $\text{HCl}$ ,  $\text{SO}_2$ ,  $\text{H}_2\text{SO}_4$ ,  $\text{Cl}$ ,  $\text{HF}$ ,  $\text{SiF}_4$ ,  $\text{H}_2\text{SiF}_6$ .

Sulphurous acid is harmless in a concentration of 0.00001 to 0.0001 per 1000, but 0.0002 per 1000 has a distinctly injurious effect after one year's action; 0.001 per 1000 acts harmfully in the course of a few weeks, and 0.01 per 1000 kills plants in a few days. An  $N/200$  solution of hydrofluosilicic acid affects pines and firs very markedly if they are sprayed with it seventeen times in the course of a few days.

#### APPENDIX—TOBACCO SMOKE

Although the investigation of tobacco smoke is not, strictly speaking, a branch of air analysis, it may be of interest to include an outline of the methods employed by Pontag<sup>3</sup> in his recent work on the subject.

The chief products of interest in tobacco smoke are nicotine, pyridine, ammonia, carbon monoxide, and hydrocyanic acid. The method adopted by Pontag for their estimation is to aspirate the smoke through two bottles containing 10 per cent. sodium hydroxide solution, and then through three bottles containing 10 per cent. sulphuric acid. The alkali from the two bottles is combined, and all basic products removed by steam distillation. The residue is treated with ether to remove tarry matter, and then gradually acidified with dilute sulphuric acid, the solution being kept cool during the addition. The hydrocyanic acid is then distilled off, collected in dilute potassium hydroxide solution, and converted to Prussian blue, which is collected and weighed. Fifty g. of tobacco yielded between 12 and 4.5 mg. of Prussian blue, corresponding to approximately between 5 and 2 mg. of hydrocyanic acid, since 858.8 g. of Prussian blue correspond to 485.6 g. of hydrocyanic acid. The remaining solution is added to the contents of bottles 3, 4, and 5, the latter having been previously extracted with ether. The combined liquid is rendered alkaline, and the nicotine, pyridine, and ammonia distilled off with steam into a receiver containing acetic acid, and the distillate again subjected to steam distillation. This second distillation removes the pyridine and its homologues, together with some acetic acid, but no trace of nicotine or of ammonium acetate passes over. The

<sup>1</sup> *J. Royal Horticultural Society*, 1893, 16, 1.

<sup>2</sup> *Z. angew. Chem.*, 1901, 14, 689.

<sup>3</sup> *Z. Unters. Nähr. u. Genussm.*, 1903, 6, 646.

distillate, containing pyridine acetate and excess of acetic acid, is made alkaline, the pyridine distilled off, the distillate diluted to 500 c.c., and titrated in quantities of 100 c.c. with  $N/10$  acid, methyl orange being used as indicator. One c.c.  $N/10$  acid = 7.9 mg. pyridine. (Quantity used =  $a$  c.c.) The residual liquid, containing nicotine and ammonium acetate, is distilled with sodium hydroxide and the distillate collected in cold water; the distillation is continued until a few drops of the liquid passing over give no further precipitate with potassium-bismuth iodide. It is then diluted to 1 litre, and 200 c.c. titrated with  $N/10$  acid, using rosolic acid as indicator. (Quantity used =  $b$  c.c.) In a second portion of 200 c.c., the nicotine is precipitated with potassium-bismuth iodide after acidification with sulphuric acid. The precipitate is filtered off, brought into a glass cylinder whilst still moist, 20 c.c. of 15 per cent. sodium hydroxide solution added, and the liquid extracted with 100 c.c. of a mixture of equal volumes of alcohol and petroleum ether. After prolonged standing, 50 c.c. of the mixture are filtered off, and the contained nicotine titrated with  $N/10$  acid, using iodoeosine as indicator, according to C. Keller's method. (Quantity used =  $c$  c.c.)

The total quantities of the bases present in the total distillates are then:—

$$\begin{aligned} 5 \times c \times 16.2 \text{ mg. Nicotine,} \\ 5 \times a \times 7.9 \text{ mg. Pyridine,} \\ 5 (b - c) \times 1.7 \text{ mg. Ammonia.} \end{aligned}$$

The smoke from 100 g. of tobacco was found to contain about 1.16 g. nicotine, 0.36 g. ammonia, and 0.15 g. pyridine; approximately, 50 per cent. of the nicotine in the tobacco passed into the smoke and 22 per cent. condensed in the mouthpiece used. Experiments by Lehmann and F. Schmitt, by a method similar to the above, showed that when cigarettes were smoked to the end, and great care was taken to secure complete absorption of the products of combustion, approximately 88 per cent. of the nicotine contained in the tobacco was found in the smoke.

For the estimation of carbon monoxide in the smoke, Pontag used the method described on p. 894. One hundred g. of tobacco yielded about 4124 c.c. of carbon monoxide. The smoke from one cigarette, according to these data, yields 5 mg. of nicotine, 1.5 mg. of ammonia, 0.7 mg. of pyridine, 0.03 mg. of hydrocyanic acid, and 18 c.c. of carbon monoxide.

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# APPENDIX

THIS APPENDIX COMPRISES THE TABLES INCLUDED IN THE TEXT, AND ALSO TABLES FOR CORRECTING THE VOLUMES OF GASES TO THE NORMAL TEMPERATURE AND PRESSURE.

## CONTENTS

No. of Table.	Page.	Subject.	Page in Text.
I.	915	Table for the calibration of apparatus for volumetric analysis	37
II.	916	Table for the calibration of apparatus for volumetric analysis	38
III.	917	Table for correcting the volume of water or of dilute standard solutions to 15° C.	...
IV.	918	Dietrich's table for the absorption of nitrogen.	128
V.	919	Dietrich's table for the weight of 1 c.c. of nitrogen	129
VI.	921	Table for reducing the volume of a gas to 0° C.	...
VII.	927	Table for reducing the volume of a gas to 760 mm. pressure.	...
VIII.	933	Table of the tension of water vapour between -20° and +118° C.	...
IX.	934	Table for the conversion of volumes of gas, obtained in the gas-volumeter, into weights of active constituents	146
X.	935	Comparison of various Baumé hydrometers, for heavy liquids, with specific gravities	159
XI.	936	Table for the conversion of specific gravities into "rational" Baumé degrees	160
XII.	938	Comparison of various hydrometers, for liquids lighter than water, with specific gravities	162
XIII.	939	Table for the reduction of anemometer readings to velocity of current, expressed in feet per second	171
XIV.	939	Table for the reduction of anemometer readings to velocity of current, expressed in metres per second	172
XV.	940	Table for correction of temperature of anemometer readings to 15° C.	172
XVI.	940	Table of temperatures indicated by Seger cones	176
XVII.	941	Table for correcting the volume of gases having a calorific value of 5000 calories ( $\pm 200$ calories), per cubic metre, to 15° C. and 760 mm.	231
XVIII.	942	Specific gravities of solutions of sulphur in carbon bisulphide, and weights of sulphur dissolved	269



No. of Table.	Page.	Subject.	Page in Text.
XIX.	943	Specific gravity of solutions of sulphur dioxide in water . . . . .	305
XX.	943	Table for correcting the specific gravity of nitric acid for the contained nitric peroxide . . . . .	324
XXI.	944	Specific gravity of nitric acid . . . . .	325
XXII.	946	Temperature correction table for XXI. . . . .	327
XXIII.	947	Table for the estimation of nitrous acid in nitrous vitriol . . . . .	344
XXIV.	948	Table for calculating volumes of nitric oxide to weights of nitrogen, nitric oxide, nitrous acid, nitric acid, and sodium nitrate . . . . .	345
XXV.	949	Table for determining the specific gravity of sulphuric acid from the percentage content . . . . .	348
XXVI.	951	Specific gravity of sulphuric acid solutions . . . . .	350
XXVII.	956	Influence of temperature on the specific gravity of sulphuric acid . . . . .	355
XXVIII.	957	Reduction of hydrometer readings for sulphuric acid to 15° C. . . . .	357
XXIX.	958	Melting points of sulphuric acid . . . . .	358
XXX.	958	Boiling points of sulphuric acid . . . . .	358
XXXI.	959	Specific gravity of fuming sulphuric acid, and percentage content of sulphur trioxide . . . . .	386
XXXII.	960	Table for finding the percentage of sulphur trioxide in oleum from the total sulphur trioxide . . . . .	394
XXXIII.	961	Table for finding the percentage of free sulphur trioxide in oleum from the total acidity, calculated as sulphuric acid . . . . .	395
XXXIV.	961	Specific gravity of solutions of sodium chloride . . . . .	397
XXXV.	962	Specific gravity of hydrochloric acid . . . . .	412
XXXVI.	963	Specific gravity of solutions of sodium carbonate at 15° C. . . . .	447
XXXVII.	964	Specific gravity of solutions of sodium carbonate in degrees Twaddell . . . . .	448
XXXVIII.	965	Specific gravity of concentrated solutions of sodium carbonate at 30° C. . . . .	449
XXXIX.	965	Influence of temperature on the specific gravity of sodium carbonate solutions . . . . .	449
XL.	966	English, German, and French commercial alkalimetric degrees . . . . .	452
XLI.	967	Specific gravity of solutions of sodium hydroxide . . . . .	464
XLII.	967	Specific gravity and composition of milk of lime . . . . .	464
XLIII.	968	Table of the percentage of chlorine corresponding to French "degrees" . . . . .	499
XLIV.	968	Specific gravity of bleach solutions . . . . .	500
XLV.	969	Weight of 1 c.c. of chlorine in milligrams . . . . .	508
XLVI.	970	Pressure and specific gravity of liquid chlorine . . . . .	519
XLVII.	971	Table of the weight of substance to be weighed out for the determination of calcium carbonate in limestone . . . . .	661
XLVIII.	973	Specific gravity of cement . . . . .	701
XLIX.	973	Table of hardness of water, as determined by Clark's soap test . . . . .	741
L.	974	Table giving correction for titrations with silver nitrate solution by Mohr's method . . . . .	750
LI.	974	Table giving the percentage of oxygen in dissolved air, at various temperatures . . . . .	787
LII.	975	Table for the determination of carbon dioxide in air by Lunge and Zeckendorf's method . . . . .	876
LIII.	975	Maximum moisture content in 1 cubic metre of air, in grams . . . . .	877

TABLE I. (*Text*, p. 37.)  
Table for the Calibration of Apparatus for Volumetric Analysis.

Weight in mg. to be added for 1000 c.c.; the cubic coefficient of expansion of glass = 0.000027 per ° C. Normal temperature, 15°. Water temperature, from 5°-30°. Height of barometer, 760 mm. Temperature of the air, 15°. Mean pressure of aqueous vapour = 8 mg. per litre.

Temp.	°0	°1	°2	°3	°4	°5	°6	°7	°8	°9	Temp.
5	1341	1340	1339	1338	1338	1338	1338	1338	1338	1338	5
6	1338	1339	1340	1341	1342	1343	1344	1345	1346	1348	6
7	1350	1352	1354	1356	1358	1360	1363	1366	1369	1372	7
8	1376	1380	1384	1388	1392	1396	1400	1404	1408	1412	8
9	1417	1421	1426	1431	1436	1442	1447	1452	1458	1464	9
10	1471	1477	1483	1489	1496	1503	1510	1517	1524	1531	10
11	1539	1547	1555	1563	1571	1579	1587	1595	1603	1611	11
12	1619	1628	1637	1646	1655	1664	1673	1683	1693	1703	12
13	1713	1723	1733	1743	1753	1764	1775	1786	1797	1808	13
14	1819	1830	1841	1853	1865	1877	1889	1901	1913	1925	14
15	1937	1949	1962	1975	1988	2001	2014	2027	2040	2053	15
16	2066	2080	2094	2108	2122	2136	2150	2164	2178	2193	16
17	2208	2223	2238	2253	2268	2283	2298	2313	2328	2344	17
18	2360	2376	2392	2408	2424	2440	2457	2474	2491	2508	18
19	2525	2542	2559	2576	2593	2610	2627	2645	2663	2681	19
20	2699	2717	2735	2753	2771	2789	2807	2826	2845	2864	20
21	2883	2902	2921	2940	2959	2978	2998	3018	3038	3058	21
22	3078	3098	3118	3138	3158	3178	3199	3220	3241	3262	22
23	3283	3304	3325	3346	3367	3388	3410	3432	3454	3476	23
24	3498	3520	3542	3564	3586	3609	3632	3655	3678	3701	24
25	3724	3747	3770	3793	3816	3839	3862	3886	3910	3934	25
26	3958	3982	4006	4030	4054	4078	4102	4127	4152	4177	26
27	4202	4227	4252	4277	4302	4327	4352	4377	4403	4429	27
28	4455	4481	4507	4533	4559	4585	4611	4637	4663	4689	28
29	4716	4743	4770	4797	4824	4851	4878	4905	4932	4959	29
30	4987	5014	5041	5069	5097	5125	5153	5181	5210	5239	30

TABLE II. (*Text*, p. 38.)

## Table for the Calibration of Apparatus for Volumetric Analysis.

Correction of the Values in TABLE I. in mg. for 1000 c.c. for atmospheric pressure, 650-790 mm., and temperature of the air, 5°-31° C.

Mm.	660.	660.	670.	680.	690.	700.	710.	720.	730.	740.	750.	760.	770.	780.	790.	Mm.
Temp. 5°	-121	-106	-91	-77	-62	-47	-32	-18	-3	+11	+26	+41	+55	+70	+84	5°
6	-124	-109	-95	-80	-66	-51	-36	-22	-7	+7	+22	+37	+51	+66	+80	6
7	-128	-113	-99	-84	-70	-55	-40	-26	11	+3	+18	+32	+47	+61	+76	7
8	-131	-116	-102	-87	-73	-58	-44	-29	15	0	+14	+28	+43	+57	+72	8
9	-135	-120	-106	-91	-77	-62	-48	-33	19	-4	+10	+24	+38	+53	+67	9
10	-138	-124	-109	-95	-80	-66	-52	-37	23	8	+6	+20	+34	+49	+63	10
11	-141	-127	-112	-98	-84	-70	-56	-41	-27	-12	+2	+16	+30	+45	+59	11
12	-145	-131	-116	-102	-88	-74	-60	-45	-31	-16	-2	+12	+26	+41	+55	12
13	-148	-134	-119	-105	-91	-77	-63	-49	-34	-20	-6	+8	+22	+36	+50	13
14	-152	-138	-123	-108	-94	-81	-67	-53	-38	-24	-10	+4	+18	+32	+46	14
15	-155	-141	-127	-112	-98	-85	-71	-57	-42	-28	-14	0	+14	+28	+42	15
16	-158	-144	-130	-116	-102	-88	-74	-60	-46	-32	-18	-4	+10	+24	+38	16
17	-161	-147	-133	-120	-106	-92	-78	-64	-50	-36	-22	-8	+6	+20	+34	17
18	-165	-151	-137	-123	-109	-95	-81	-67	-53	-39	-25	-11	+3	+16	+30	18
19	-168	-154	-140	-127	-113	-99	-85	-71	-57	-43	-29	-15	+1	+12	+26	19
20	-171	-157	-143	-130	-116	-102	-88	-74	-61	-47	-33	-19	-5	+8	+22	20
21	-174	-161	-147	-133	-119	-105	-91	-78	-64	-51	-37	-23	-9	+4	+18	21
22	-177	-164	-150	-137	-123	-109	-95	-81	-68	-54	-40	-26	-13	+1	+14	22
23	-181	-167	-154	-140	-126	-112	-98	-85	-71	-58	-44	-30	-16	-3	+11	23
24	-184	-171	-157	-144	-130	-116	-102	-88	-75	-61	-47	-33	-20	-6	+7	24
25	-187	-174	-160	-147	-133	-119	-105	-92	-78	-65	-51	-37	-24	-10	+3	25
26	-190	-177	-163	-150	-136	-122	-108	-95	-82	-68	-55	-41	-28	-14	-1	26
27	-193	-180	-166	-153	-139	-125	-112	-98	-85	-71	-58	-45	-31	-18	+4	27
28	-197	-184	-170	-157	-143	-129	-116	-102	-89	-75	-62	-48	-35	-21	+8	28
29	-200	-187	-173	-160	-146	-132	-119	-105	-92	-78	-65	-52	-38	-25	+11	29
30	-203	-190	-176	-163	-149	-135	-122	-109	-95	-82	-69	-56	-42	-29	+15	30
31	-206	-193	-179	-166	-152	-138	-125	-112	-99	-86	-73	-60	-46	-33	+19	31

TABLE III.

Table for correcting the Volume of Water or of Dilute Standard Solutions ( $N/5$  or more dilute) to  $15^{\circ}$ .

This is a more convenient form, for practical work, of the Table on p. 46.  
If the temperature of the solution is  $t^{\circ}$ , it is multiplied by the factor in column  $a$ , to correct the volume to  $15^{\circ}$ ; or the value in column  $b$  is deducted from the observed volume.

$t^{\circ}$ .	$a$ . Factor.	$b$ . Value in c.c. to be deducted from each 100 c.c.	$t^{\circ}$ .	$a$ . Factor.	$b$ . Value in c.c. to be deducted from each 100 c.c.
15	1,0000	0	23	0,9986	0,135
16	0,9999	0,013	24	0,9984	0,156
17	0,9997	0,027	25	0,9982	0,179
18	0,9996	0,042	26	0,9980	0,202
19	0,9994	0,059	27	0,9977	0,227
20	0,9992	0,076	28	0,9975	0,252
21	0,9991	0,095	29	0,9972	0,278
22	0,9989	0,114	30	0,9970	0,305

TABLE IV. (Text, p. 128.)

## Dietrich's Table for the Absorption of Nitrogen.

*In 60 c.c. generating liquid (50 c.c. hypobromite solution and 10 c.c. water), the hypobromite solution having the sp. gr. 1.1, and of such strength that 50 c.c. correspond to 200 mg. N when from 1 to 100 c.c. of gas are evolved.*

Liberated . .	1	2	3	4	5	6	7	8	9	10
Absorbed . .	0.06	0.08	0.11	0.13	0.16	0.18	0.21	0.23	0.26	0.28
Liberated . .	11	12	13	14	15	16	17	18	19	20
Absorbed . .	0.31	0.33	0.36	0.38	0.41	0.43	0.46	0.48	0.51	0.53
Liberated . .	21	22	23	24	25	26	27	28	29	30
Absorbed . .	0.56	0.58	0.61	0.63	0.66	0.68	0.71	0.73	0.76	0.78
Liberated . .	31	32	33	34	35	36	37	38	39	40
Absorbed . .	0.81	0.83	0.86	0.88	0.91	0.93	0.96	0.98	1.01	1.03
Liberated . .	41	42	43	44	45	46	47	48	49	50
Absorbed . .	1.06	1.08	1.11	1.13	1.16	1.18	1.21	1.23	1.26	1.28
Liberated . .	51	52	53	54	55	56	57	58	59	60
Absorbed . .	1.31	1.33	1.36	1.38	1.41	1.43	1.46	1.48	1.51	1.53
Liberated . .	61	62	63	64	65	66	67	68	69	70
Absorbed . .	1.56	1.58	1.61	1.63	1.66	1.68	1.71	1.73	1.76	1.78
Liberated . .	71	72	73	74	75	76	77	78	79	80
Absorbed . .	1.81	1.83	1.86	1.88	1.91	1.93	1.96	1.98	2.01	2.03
Liberated . .	81	82	83	84	85	86	87	88	89	90
Absorbed . .	2.06	2.08	2.11	2.13	2.16	2.18	2.21	2.23	2.26	2.28
Liberated . .	91	92	93	94	95	96	97	98	99	100
Absorbed . .	2.31	2.33	2.36	2.38	2.41	2.43	2.46	2.48	2.51	2.53

*In Milligrams, at pressures from 720 to 770 Millimetres of Mercury, and 1 emperatures from 10° to 25° C.*

Temp. in degrees Centigrade.	● Millimetres.													
	720	722	724	726	728	730	732	734	736	738	740	742	744	
10	1.13380	1.13699	1.14018	1.14337	1.14656	1.14975	1.15294	1.15613	1.15932	1.16251	1.16570	1.16889	1.17208	
11	1.12881	1.13199	1.13517	1.13835	1.14153	1.14471	1.14789	1.15107	1.15424	1.15742	1.16060	1.16378	1.16696	
12	1.12376	1.12693	1.13010	1.13326	1.13643	1.13960	1.14277	1.14593	1.14910	1.15227	1.15543	1.15860	1.16177	
13	1.11875	1.12191	1.12506	1.12822	1.13138	1.13454	1.13769	1.14085	1.14401	1.14716	1.15032	1.15348	1.15663	
14	1.11369	1.11684	1.11999	1.12313	1.12628	1.12942	1.13257	1.13572	1.13886	1.14201	1.14515	1.14830	1.15145	
15	1.10859	1.11172	1.11486	1.11799	1.12113	1.12426	1.12739	1.13053	1.13366	1.13680	1.13993	1.14306	1.14620	
16	1.10346	1.10658	1.10971	1.11283	1.11596	1.11908	1.12220	1.12533	1.12845	1.13158	1.13470	1.13782	1.14095	
17	1.09822	1.10139	1.10450	1.10761	1.11073	1.11384	1.11695	1.12006	1.12317	1.12629	1.12940	1.13251	1.13562	
18	1.09304	1.09614	1.09924	1.10234	1.10544	1.10854	1.11165	1.11475	1.11785	1.12095	1.12405	1.12715	1.13025	
19	1.08774	1.09083	1.09392	1.09702	1.10011	1.10320	1.10629	1.10938	1.11248	1.11557	1.11866	1.12175	1.12484	
20	1.08246	1.08554	1.08862	1.09170	1.09478	1.09786	1.10094	1.10402	1.10710	1.11018	1.11327	1.11635	1.11943	
21	1.07708	1.08015	1.08322	1.08629	1.08936	1.09243	1.09550	1.09857	1.10165	1.10472	1.10779	1.11086	1.11393	
22	1.07166	1.07472	1.07778	1.08084	1.08390	1.08696	1.09002	1.09308	1.09614	1.09921	1.10277	1.10583	1.10889	
23	1.06616	1.06921	1.07226	1.07531	1.07836	1.08141	1.08446	1.08751	1.09056	1.09361	1.09666	1.09971	1.10276	
24	1.06061	1.06365	1.06669	1.06973	1.07277	1.07581	1.07885	1.08189	1.08493	1.08796	1.09100	1.09404	1.09708	
25	1.05499	1.05801	1.06104	1.06407	1.06710	1.07013	1.07316	1.07619	1.07922	1.08225	1.08528	1.08831	1.09134	

# APPENDIX

Dietrich's Table for the Weight of 1 c.c. of Nitrogen—Continued.

Temp. in degrees Centigrade.	Millimetres.													
	748	750	752	754	756	758	760	762	764	766	768	770		
10	1.17527	1.17846	1.18165	1.18484	1.18803	1.19122	1.19441	1.19760	1.20079	1.20398	1.20717	1.21036	1.21355	
11	1.17014	1.17332	1.17650	1.17968	1.18286	1.18603	1.18921	1.19239	1.19557	1.19875	1.20193	1.20511	1.20829	
12	1.16493	1.16810	1.17127	1.17444	1.17760	1.18077	1.18394	1.18710	1.19027	1.19344	1.19660	1.19977	1.20294	
13	1.15979	1.16295	1.16611	1.16926	1.17242	1.17558	1.17873	1.18189	1.18505	1.18820	1.19136	1.19452	1.19768	
14	1.15459	1.15774	1.16088	1.16403	1.16718	1.17032	1.17347	1.17661	1.17976	1.18291	1.18605	1.18920	1.19234	
15	1.14933	1.15247	1.15560	1.15873	1.16187	1.16500	1.16814	1.17127	1.17440	1.17754	1.18067	1.18381	1.18694	
16	1.14407	1.14720	1.15032	1.15344	1.15657	1.15969	1.16282	1.16594	1.16906	1.17219	1.17531	1.17844	1.18156	
17	1.13873	1.14185	1.14496	1.14807	1.15118	1.15429	1.15741	1.16052	1.16365	1.16674	1.16985	1.17297	1.17608	
18	1.13335	1.13645	1.13955	1.14266	1.14576	1.14886	1.15196	1.15506	1.15816	1.16126	1.16436	1.16746	1.17056	
19	1.12794	1.13103	1.13412	1.13721	1.14030	1.14340	1.14649	1.14958	1.15267	1.15576	1.15886	1.16195	1.16504	
20	1.12251	1.12559	1.12867	1.13175	1.13483	1.13791	1.13999	1.14408	1.14716	1.15024	1.15332	1.15640	1.15948	
21	1.11700	1.12007	1.12314	1.12621	1.12928	1.13236	1.13543	1.13850	1.14157	1.14464	1.14771	1.15078	1.15385	
22	1.11145	1.11451	1.11757	1.12063	1.12369	1.12675	1.12982	1.13288	1.13594	1.13900	1.14296	1.14512	1.14818	
23	1.10581	1.10886	1.11191	1.11496	1.11801	1.12106	1.12411	1.12716	1.13021	1.13326	1.13631	1.13936	1.14241	
24	1.10012	1.10316	1.10620	1.10924	1.11228	1.11532	1.11835	1.12139	1.12443	1.12747	1.13051	1.13355	1.13659	
25	1.09437	1.09740	1.10043	1.10346	1.10649	1.10952	1.11255	1.11558	1.11861	1.12164	1.12467	1.12770	1.13073	

TABLE VI.

Table for reducing the Volume of a Gas to 0° C.

0°	1°	2°	3°	4°	5°	6°	7°	8°	9°	10°
1	0.996	0.993	0.989	0.986	0.982	0.978	0.975	0.972	0.968	0.965
2	1.993	1.985	1.978	1.971	1.964	1.957	1.950	1.943	1.936	1.929
3	2.989	2.978	2.967	2.957	2.946	2.936	2.925	2.915	2.904	2.894
4	3.985	3.971	3.956	3.942	3.928	3.914	3.900	3.886	3.872	3.859
5	4.982	4.964	4.946	4.928	4.910	4.896	4.875	4.858	4.841	4.824
6	5.978	5.956	5.935	5.913	5.892	5.871	5.850	5.830	5.809	5.788
7	6.974	6.949	6.924	6.899	6.874	6.850	6.825	6.801	6.777	6.753
8	7.970	7.942	7.913	7.885	7.856	7.828	7.800	7.773	7.745	7.718
9	8.967	8.934	8.902	8.870	8.838	8.807	8.775	8.744	8.713	8.682
10	9.963	9.927	9.891	9.856	9.820	9.785	9.750	9.716	9.681	9.647
11	10.96	10.92	10.88	10.84	10.80	10.76	10.73	10.69	10.65	10.61
12	11.96	11.91	11.87	11.83	11.78	11.74	11.70	11.66	11.62	11.57
13	12.95	12.91	12.86	12.81	12.76	12.72	12.68	12.63	12.59	12.54
14	13.95	13.90	13.85	13.80	13.75	13.70	13.65	13.60	13.55	13.50
15	14.95	14.89	14.84	14.78	14.73	14.68	14.63	14.57	14.52	14.47
16	15.94	15.88	15.83	15.77	15.71	15.66	15.60	15.55	15.49	15.43
17	16.94	16.87	16.82	16.75	16.69	16.64	16.58	16.52	16.46	16.40
18	17.93	17.87	17.81	17.74	17.67	17.61	17.55	17.49	17.43	17.36
19	18.93	18.86	18.79	18.72	18.65	18.59	18.53	18.46	18.39	18.33
20	19.93	19.85	19.78	19.71	19.64	19.57	19.50	19.43	19.36	19.29
21	20.93	20.84	20.77	20.69	20.62	20.55	20.48	20.40	20.33	20.26
22	21.92	21.84	21.76	21.68	21.60	21.53	21.45	21.37	21.30	21.22
23	22.92	22.83	22.75	22.66	22.58	22.51	22.43	22.35	22.26	22.18
24	23.92	23.82	23.74	23.65	23.56	23.48	23.40	23.32	23.23	23.15
25	24.91	24.81	24.73	24.64	24.55	24.46	24.38	24.29	24.20	24.11
26	25.91	25.81	25.72	25.62	25.53	25.44	25.35	25.26	25.17	25.08
27	26.90	26.80	26.71	26.61	26.52	26.42	26.33	26.23	26.13	26.04
28	27.90	27.79	27.69	27.59	27.50	27.40	27.30	27.20	27.10	27.01
29	28.90	28.78	28.68	28.58	28.48	28.38	28.28	28.17	28.07	27.97
30	29.89	29.78	29.67	29.57	29.46	29.36	29.25	29.15	29.04	28.94
31	30.89	30.77	30.66	30.55	30.44	30.34	30.23	30.12	30.01	29.91
32	31.88	31.76	31.65	31.54	31.42	31.32	31.20	31.09	30.98	30.87
33	32.88	32.76	32.64	32.52	32.40	32.30	32.18	32.06	31.94	31.84
34	33.88	33.75	33.63	33.51	33.38	33.27	33.15	33.03	32.91	32.80
35	34.87	34.74	34.62	34.50	34.37	34.25	34.13	34.01	33.88	33.77
36	35.87	35.74	35.61	35.48	35.35	35.23	35.10	34.98	34.85	34.73
37	36.87	36.73	36.60	36.47	36.33	36.21	36.08	35.95	35.82	35.70
38	37.86	37.72	37.59	37.45	37.32	37.19	37.05	36.92	36.79	36.66
39	38.86	38.71	38.58	38.44	38.30	38.16	38.03	37.89	37.75	37.62
40	39.85	39.71	39.56	39.42	39.28	39.14	39.00	38.86	38.72	38.59
41	40.85	40.70	40.55	40.41	40.26	40.12	39.98	39.83	39.69	39.55
42	41.85	41.69	41.54	41.39	41.24	41.10	40.95	40.80	40.66	40.52
43	42.84	42.68	42.53	42.38	42.22	42.08	41.93	41.78	41.62	41.48
44	43.84	43.68	43.52	43.37	43.20	43.05	42.90	42.75	42.59	42.45
45	44.84	44.67	44.51	44.35	44.19	44.03	43.88	43.72	43.56	43.41
46	45.83	45.66	45.50	45.34	45.17	45.01	44.85	44.69	44.53	44.38
47	46.83	46.65	46.48	46.32	46.15	45.99	45.83	45.66	45.50	45.34
48	47.83	47.65	47.48	47.31	47.13	46.97	46.80	46.63	46.47	46.31
49	48.82	48.64	48.47	48.29	48.12	47.95	47.78	47.60	47.44	47.27
50	49.82	49.64	49.46	49.28	49.10	48.93	48.75	48.58	48.41	48.24



Table for reducing the Volume of a Gas to 0° C.—Continued.

0°	1°	2°	3°	4°	5°	6°	7°	8°	9°	10°
51	50.82	50.63	50.45	50.26	50.08	49.91	49.73	49.55	49.38	49.21
52	51.81	51.62	51.44	51.25	51.06	50.89	50.70	50.52	50.35	50.17
53	52.81	52.62	52.43	52.24	52.05	51.87	51.68	51.49	51.31	51.13
54	53.81	53.61	53.42	53.22	53.03	52.84	52.65	52.46	52.28	52.10
55	54.80	54.60	54.41	54.21	54.01	53.82	53.63	53.44	53.25	53.06
56	55.80	55.60	55.40	55.19	54.99	54.80	54.60	54.41	54.22	54.03
57	56.80	56.59	56.39	56.18	55.97	55.78	55.58	55.38	55.19	54.99
58	57.79	57.58	57.37	57.16	56.95	56.76	56.55	56.35	56.15	55.96
59	58.79	58.57	58.37	58.15	57.93	57.74	57.53	57.32	57.12	56.92
60	59.78	59.56	59.35	59.13	58.92	58.71	58.50	58.30	58.09	57.88
61	60.78	60.56	60.34	60.12	59.90	59.69	59.48	59.27	59.06	58.85
62	61.78	61.55	61.33	61.10	60.88	60.67	60.45	60.24	60.03	59.81
63	62.77	62.54	62.32	62.09	61.86	61.65	61.43	61.21	60.99	60.77
64	63.77	63.53	63.31	63.07	62.84	62.63	62.40	62.18	61.96	61.74
65	64.76	64.53	64.30	64.06	63.83	63.61	63.38	63.15	62.93	62.70
66	65.76	65.52	65.29	65.04	64.81	64.58	64.35	64.13	63.89	63.67
67	66.75	66.51	66.27	66.03	65.79	65.56	65.33	65.10	64.86	64.63
68	67.75	67.50	67.26	67.02	66.77	66.54	66.30	66.07	65.83	65.60
69	68.75	68.50	68.25	68.01	67.75	67.52	67.28	67.04	66.80	66.56
70	69.74	69.49	69.24	68.99	68.74	68.50	68.25	68.01	67.77	67.53
71	70.74	70.48	70.23	69.98	69.72	69.48	69.23	68.98	68.74	68.49
72	71.74	71.48	71.22	70.96	70.70	70.46	70.20	69.95	69.71	69.46
73	72.73	72.47	72.21	71.95	71.69	71.44	71.18	70.93	70.67	70.42
74	73.73	73.46	73.20	72.93	72.66	72.41	72.15	71.90	71.64	71.39
75	74.72	74.45	74.19	73.92	73.65	73.39	73.13	72.87	72.61	72.35
76	75.72	75.45	75.18	74.90	74.63	74.37	74.10	73.84	73.58	73.32
77	76.72	76.44	76.17	75.89	75.61	75.35	75.08	74.81	74.55	74.28
78	77.71	77.43	77.15	76.87	76.59	76.33	76.05	75.78	75.51	75.25
79	78.71	78.42	78.14	77.86	77.58	77.31	77.03	76.75	76.48	76.21
80	79.70	79.42	79.13	78.85	78.56	78.28	78.00	77.73	77.45	77.18
81	80.70	80.41	80.12	79.83	79.54	79.26	78.98	78.70	78.42	78.14
82	81.69	81.40	81.11	80.82	80.52	80.24	79.95	79.67	79.39	79.11
83	82.69	82.39	82.10	81.81	81.51	81.22	80.93	80.64	80.36	80.07
84	83.69	83.39	83.09	82.79	82.49	82.20	81.90	81.61	81.32	81.04
85	84.68	84.38	84.08	83.78	83.47	83.17	82.88	82.58	82.29	82.00
86	85.68	85.37	85.07	84.76	84.45	84.15	83.85	83.55	83.26	82.97
87	86.68	86.37	86.06	85.75	85.43	85.13	84.83	84.53	84.23	83.93
88	87.67	87.36	87.05	86.73	86.42	86.11	85.80	85.50	85.20	84.90
89	88.67	88.35	88.04	87.72	87.40	87.09	86.78	86.47	86.16	85.86
90	89.67	89.34	89.02	88.70	88.38	88.07	87.75	87.44	87.13	86.82
91	90.66	90.34	90.01	89.69	89.36	89.05	88.73	88.41	88.10	87.79
92	91.66	91.33	91.00	90.67	90.34	90.03	89.70	89.38	89.07	88.75
93	92.66	92.32	91.99	91.66	91.33	91.01	90.68	90.36	90.03	89.72
94	93.65	93.31	92.98	92.64	92.31	91.98	91.65	91.33	91.00	90.68
95	94.65	94.31	93.97	93.63	93.29	92.96	92.63	92.30	91.97	91.65
96	95.65	95.30	94.96	94.61	94.27	93.94	93.60	93.27	92.94	92.61
97	96.64	96.29	95.95	95.60	95.25	94.92	94.58	94.24	93.91	93.57
98	97.64	97.28	96.93	96.58	96.24	95.90	95.55	95.21	94.87	94.54
99	98.64	98.27	97.92	97.57	97.22	96.87	96.53	96.18	95.84	95.50
100	99.63	99.27	98.91	98.56	98.20	97.85	97.50	97.16	96.81	96.47

Table for reducing the Volume of a Gas to 0° C.—Continued.

0°	11°	12°	13°	14°	15°	16°	17°	18°	19°	20°
1	0.961	0.958	0.955	0.951	0.948	0.945	0.941	0.938	0.935	0.932
2	1.923	1.916	1.909	1.903	1.896	1.889	1.883	1.876	1.869	1.864
3	2.884	2.874	2.864	2.854	2.844	2.834	2.824	2.815	2.805	2.795
4	3.845	3.832	3.818	3.805	3.792	3.779	3.766	3.753	3.740	3.727
5	4.807	4.790	4.773	4.757	4.740	4.724	4.707	4.691	4.675	4.659
6	5.768	5.747	5.728	5.708	5.688	5.668	5.648	5.629	5.609	5.591
7	6.729	6.705	6.682	6.659	6.636	6.613	6.590	6.567	6.544	6.523
8	7.690	7.663	7.637	7.610	7.584	7.558	7.531	7.506	7.479	7.454
9	8.652	8.621	8.591	8.562	8.532	8.502	8.472	8.444	8.414	8.386
10	9.613	9.579	9.546	9.513	9.480	9.447	9.414	9.382	9.349	9.318
11	10.57	10.53	10.50	10.46	10.43	10.39	10.35	10.32	10.28	10.25
12	11.53	11.49	11.45	11.42	11.38	11.33	11.30	11.26	11.21	11.18
13	12.49	12.45	12.41	12.36	12.32	12.28	12.24	12.20	12.15	12.11
14	13.45	13.41	13.36	13.31	13.27	13.22	13.17	13.13	13.08	13.04
15	14.42	14.37	14.32	14.27	14.22	14.17	14.12	14.07	14.02	13.97
16	15.38	15.32	15.27	15.22	15.17	15.11	15.06	15.01	14.96	14.91
17	16.34	16.28	16.23	16.17	16.12	16.06	16.00	15.95	15.89	15.84
18	17.30	17.24	17.18	17.12	17.06	17.00	16.94	16.89	16.82	16.76
19	18.26	18.20	18.14	18.07	18.01	17.95	17.89	17.83	17.76	17.70
20	19.23	19.16	19.09	19.03	18.96	18.89	18.83	18.76	18.69	18.64
21	20.19	20.12	20.04	19.98	19.91	19.84	19.77	19.70	19.62	19.57
22	21.15	21.08	21.00	20.93	20.86	20.78	20.71	20.64	20.56	20.50
23	22.11	22.03	21.95	21.88	21.80	21.73	21.65	21.58	21.50	21.43
24	23.07	22.99	22.91	22.83	22.75	22.67	22.59	22.51	22.43	22.37
25	24.03	23.95	23.86	23.78	23.70	23.61	23.54	23.45	23.37	23.30
26	25.00	24.91	24.81	24.73	24.65	24.56	24.48	24.39	24.30	24.23
27	25.96	25.87	25.77	25.69	25.60	25.50	25.42	25.33	25.23	25.16
28	26.92	26.82	26.72	26.64	26.54	26.45	26.36	26.25	26.17	26.09
29	27.88	27.78	27.68	27.59	27.49	27.39	27.30	27.20	27.10	27.02
30	28.84	28.74	28.64	28.54	28.44	28.34	28.24	28.15	28.05	27.95
31	29.80	29.70	29.59	29.49	29.39	29.28	29.18	29.09	28.99	28.87
32	30.76	30.66	30.55	30.44	30.34	30.23	30.12	30.03	29.92	29.81
33	31.72	31.61	31.50	31.39	31.28	31.17	31.06	30.97	30.86	30.74
34	32.68	32.57	32.46	32.34	32.23	32.12	32.01	31.90	31.79	31.68
35	33.65	33.53	33.41	33.30	33.18	33.06	32.95	32.84	32.73	32.61
36	34.61	34.49	34.37	34.25	34.13	34.01	33.89	33.78	33.66	33.54
37	35.57	35.45	35.32	35.20	35.08	34.95	34.83	34.72	34.59	34.47
38	36.53	36.40	36.28	36.15	36.02	35.90	35.77	35.66	35.53	35.40
39	37.49	37.36	37.23	37.10	36.97	36.84	36.71	36.59	36.46	36.34
40	38.45	38.32	38.18	38.05	37.92	37.79	37.66	37.53	37.40	37.27
41	39.41	39.28	39.14	39.00	38.87	38.73	38.60	38.47	38.34	38.20
42	40.37	40.24	40.09	39.95	39.82	39.68	39.54	39.41	39.27	39.13
43	41.33	41.19	41.05	40.90	40.76	40.62	40.48	40.35	40.21	40.07
44	42.30	42.15	42.00	41.86	41.71	41.57	41.43	41.28	41.14	41.00
45	43.26	43.11	42.95	42.81	42.66	42.51	42.37	42.22	42.08	41.93
46	44.22	44.07	43.91	43.76	43.61	43.46	43.31	43.16	43.01	42.86
47	45.18	45.03	44.86	44.71	44.56	44.40	44.25	44.10	43.94	43.79
48	46.14	45.98	45.82	45.66	45.50	45.35	45.19	45.04	44.88	44.72
49	47.10	46.94	46.77	46.61	46.45	46.29	46.13	45.97	45.81	45.65
50	48.07	47.90	47.73	47.57	47.40	47.24	47.07	46.91	46.75	46.59

\* Table for reducing the Volume of a Gas to 0° C.—Continued.

0°	11°	12°	13°	14°	15°	16°	17°	18°	19°	20°
51	49.03	48.86	48.69	48.52	48.35	48.18	48.01	47.85	47.68	47.52
52	49.99	49.82	49.64	49.47	49.30	49.13	48.95	48.79	48.62	48.45
53	50.95	50.77	50.59	50.42	50.24	50.07	49.89	49.72	49.55	49.38
54	51.91	51.73	51.55	51.37	51.19	51.02	50.84	50.66	50.49	50.32
55	52.87	52.69	52.50	52.33	52.14	51.96	51.78	51.60	51.43	51.25
56	53.84	53.65	53.46	53.28	53.09	52.91	52.72	52.54	52.36	52.18
57	54.80	54.61	54.41	54.23	54.04	53.86	53.68	53.48	53.29	53.11
58	55.76	55.56	55.37	55.18	54.98	54.80	54.60	54.42	54.23	54.04
59	56.72	56.52	56.32	56.13	55.93	55.74	55.54	55.35	55.16	54.97
60	57.68	57.47	57.28	57.08	56.88	56.68	56.48	56.29	56.09	55.91
61	58.64	58.43	58.23	58.03	57.83	57.63	57.42	57.23	57.02	56.84
62	59.60	59.39	59.19	58.98	58.78	58.57	58.36	58.17	57.96	57.77
63	60.56	60.35	60.14	59.93	59.72	59.52	59.30	59.11	58.90	58.71
64	61.53	61.31	61.10	60.88	60.67	60.46	60.25	60.04	59.83	59.64
65	62.49	62.26	62.05	61.84	61.62	61.40	61.19	60.98	60.77	60.57
66	63.45	63.22	63.01	62.79	62.57	62.35	62.13	61.92	61.70	61.50
67	64.41	64.18	63.96	63.74	63.52	63.29	63.07	62.86	62.63	62.43
68	65.37	65.13	64.92	64.69	64.46	64.23	64.01	63.80	63.57	63.36
69	66.33	66.09	65.87	65.64	65.41	65.18	64.95	64.73	64.50	64.30
70	67.29	67.05	66.82	66.59	66.36	66.13	65.90	65.67	65.44	65.23
71	68.25	68.01	67.77	67.54	67.31	67.07	66.84	66.61	66.38	66.16
72	69.21	68.97	68.73	68.49	68.26	68.02	67.78	67.55	67.31	67.09
73	70.17	69.92	69.68	69.44	69.20	68.96	68.72	68.49	68.26	68.03
74	71.14	70.88	70.64	70.40	70.15	69.91	69.66	69.42	69.18	68.96
75	72.10	71.84	71.59	71.35	71.10	70.85	70.61	70.37	70.12	69.89
76	73.06	72.80	72.55	72.30	72.05	71.80	71.55	71.30	71.05	70.82
77	74.02	73.76	73.51	73.25	73.00	72.74	72.49	72.24	71.98	71.75
78	74.98	74.71	74.46	74.20	73.94	73.69	73.43	73.18	72.92	72.68
79	75.94	75.67	75.41	75.15	74.89	74.63	74.37	74.11	73.85	73.61
80	76.90	76.63	76.37	76.10	75.84	75.58	75.31	75.06	74.79	74.54
81	77.86	77.59	77.32	77.05	76.79	76.52	76.25	76.00	75.73	75.47
82	78.82	78.55	78.28	78.00	77.74	77.47	77.19	76.94	76.66	76.40
83	79.78	79.50	79.23	78.95	78.68	78.41	78.13	77.87	77.60	77.34
84	80.75	80.46	80.19	79.91	79.63	79.35	79.08	78.81	78.53	78.27
85	81.71	81.42	81.14	80.86	80.58	80.30	80.02	79.75	79.47	79.20
86	82.67	82.38	82.10	81.81	81.53	81.24	80.96	80.69	80.40	80.13
87	83.63	83.33	83.05	82.76	82.48	82.19	81.90	81.63	81.33	81.06
88	84.59	84.29	84.01	83.71	83.42	83.13	82.84	82.57	82.27	81.99
89	85.56	85.25	84.96	84.66	84.37	84.08	83.78	83.50	83.22	82.93
90	86.52	86.21	85.92	85.62	85.32	85.02	84.72	84.44	84.14	83.86
91	87.48	87.17	86.87	86.57	86.27	85.96	85.66	85.38	85.07	84.79
92	88.44	88.13	87.83	87.52	87.22	86.91	86.60	86.32	86.01	85.72
93	89.40	89.08	88.78	88.47	88.16	87.85	87.54	87.25	86.95	86.66
94	90.36	90.04	89.73	89.42	89.11	88.80	88.49	88.19	87.88	87.59
95	91.33	91.00	90.68	90.38	90.06	89.74	89.43	89.13	88.82	88.52
96	92.29	91.96	91.64	91.33	91.01	90.69	90.37	90.07	89.75	89.45
97	93.25	92.92	92.59	92.28	91.96	91.63	91.31	91.00	90.68	90.38
98	94.21	93.87	93.55	93.23	92.90	92.58	92.25	91.94	91.62	91.31
99	95.17	94.83	94.50	94.18	93.85	93.52	93.19	92.88	92.55	92.24
100	96.13	95.79	95.46	95.13	94.80	94.47	94.14	93.82	93.49	93.18

Table for reducing the Volume of a Gas to 0° C.—Continued.

0°	21°	22°	23°	24°	25°	26°	27°	28°	29°
1	0.929	0.926	0.922	0.919	0.916	0.913	0.910	0.907	0.904
2	1.857	1.851	1.845	1.839	1.832	1.826	1.820	1.814	1.808
3	2.786	2.777	2.767	2.758	2.749	2.739	2.730	2.721	2.712
4	3.714	3.702	3.690	3.677	3.665	3.652	3.640	3.628	3.616
5	4.643	4.628	4.612	4.597	4.581	4.566	4.551	4.535	4.520
6	5.572	5.553	5.534	5.516	5.497	5.479	5.461	5.442	5.424
7	6.500	6.479	6.457	6.435	6.413	6.392	6.371	6.349	6.328
8	7.429	7.404	7.379	7.354	7.330	7.305	7.281	7.256	7.232
9	8.357	8.330	8.302	8.274	8.246	8.218	8.191	8.163	8.136
10	9.286	9.255	9.224	9.193	9.162	9.131	9.101	9.070	9.040
11	10.21	10.18	10.15	10.11	10.07	10.04	10.01	9.98	9.94
12	11.14	11.11	11.07	11.03	10.99	10.96	10.92	10.88	10.85
13	12.07	12.03	11.99	11.95	11.91	11.87	11.83	11.79	11.75
14	13.00	12.96	12.91	12.87	12.83	12.78	12.74	12.70	12.66
15	13.93	13.88	13.84	13.79	13.74	13.70	13.65	13.61	13.56
16	14.86	14.81	14.76	14.71	14.66	14.61	14.56	14.51	14.46
17	15.79	15.73	15.68	15.63	15.58	15.52	15.47	15.42	15.37
18	16.71	16.66	16.60	16.55	16.49	16.44	16.38	16.33	16.27
19	17.64	17.58	17.53	17.47	17.41	17.35	17.29	17.23	17.18
20	18.57	18.51	18.45	18.39	18.32	18.26	18.20	18.14	18.08
21	19.50	19.43	19.37	19.31	19.24	19.17	19.11	19.05	18.98
22	20.43	20.36	20.29	20.23	20.15	20.09	20.02	19.95	19.89
23	21.36	21.29	21.21	21.15	21.07	21.00	20.93	20.86	20.79
24	22.28	22.21	22.14	22.07	21.99	21.91	21.84	21.77	21.70
25	23.21	23.14	23.06	22.99	22.90	22.83	22.75	22.68	22.60
26	24.14	24.06	23.98	23.91	23.82	23.74	23.66	23.58	23.50
27	25.07	24.99	24.90	24.83	24.73	24.65	24.57	24.49	24.41
28	26.00	25.91	25.82	25.74	25.65	25.57	25.48	25.40	25.31
29	26.93	26.84	26.75	26.67	26.57	26.48	26.39	26.30	26.22
30	27.86	27.77	27.67	27.58	27.49	27.39	27.30	27.21	27.12
31	28.79	28.70	28.59	28.50	28.41	28.30	28.21	28.12	28.02
32	29.72	29.62	29.51	29.42	29.32	29.22	29.12	29.02	28.93
33	30.65	30.55	30.44	30.34	30.24	30.13	30.03	29.93	29.83
34	31.57	31.47	31.36	31.26	31.16	31.04	30.94	30.84	30.74
35	32.50	32.40	32.28	32.18	32.07	31.96	31.85	31.75	31.64
36	33.43	33.32	33.20	33.10	32.99	32.87	32.76	32.65	32.54
37	34.36	34.25	34.12	34.02	33.90	33.78	33.67	33.56	33.45
38	35.29	35.17	35.05	34.93	34.82	34.70	34.58	34.47	34.35
39	36.22	36.10	35.97	35.85	35.74	35.61	35.49	35.37	35.26
40	37.14	37.02	36.90	36.77	36.65	36.52	36.40	36.28	36.16
41	38.07	37.95	37.82	37.69	37.57	37.43	37.31	37.19	37.06
42	39.00	38.87	38.74	38.61	38.48	38.35	38.22	38.09	37.97
43	39.93	39.80	39.66	39.53	39.40	39.26	39.13	39.00	38.87
44	40.85	40.72	40.59	40.45	40.32	40.17	40.04	39.91	39.78
45	41.78	41.65	41.51	41.37	41.23	41.09	40.95	40.82	40.68
46	42.71	42.57	42.43	42.29	42.15	42.00	41.86	41.72	41.58
47	43.64	43.50	43.35	43.21	43.06	42.91	42.77	42.63	42.49
48	44.57	44.42	44.27	44.12	43.98	43.83	43.68	43.54	43.39
49	45.50	45.35	45.19	45.04	44.89	44.74	44.59	44.44	44.30
50	46.43	46.28	46.12	45.97	45.81	45.66	45.51	45.35	45.20

Table for reducing the Volume of a Gas to 0° C.—Continued.

0°	21°	22°	23°	24°	25°	26°	27°	28°	29°
51	47.36	47.20	47.04	46.89	46.73	46.57	46.42	46.26	46.10
52	48.29	48.13	47.96	47.81	47.64	47.49	47.33	47.16	47.01
53	49.22	49.06	48.89	48.73	48.56	48.40	48.24	48.07	47.91
54	50.14	49.98	49.81	49.65	49.48	49.31	49.15	48.98	48.82
55	51.07	50.91	50.73	50.57	50.39	50.23	50.06	49.89	49.72
56	52.00	51.83	51.65	51.49	51.31	51.14	50.97	50.79	50.62
57	52.93	52.76	52.58	52.41	52.22	52.05	51.88	51.70	51.53
58	53.86	53.68	53.50	53.32	53.14	52.97	52.79	52.61	52.43
59	54.79	54.61	54.42	54.24	54.06	53.88	53.70	53.51	53.34
60	55.72	55.53	55.34	55.16	54.97	54.79	54.61	54.42	54.24
61	56.65	56.46	56.26	56.08	55.89	55.70	55.52	55.33	55.14
62	57.58	57.38	57.19	57.00	56.80	56.62	56.43	56.23	56.05
63	58.51	58.31	58.11	57.92	57.72	57.53	57.34	57.14	56.95
64	59.42	59.23	59.03	58.84	58.64	58.44	58.25	58.05	57.86
65	60.36	60.16	59.95	59.76	59.55	59.36	59.16	58.96	58.76
66	61.29	61.08	60.87	60.68	60.47	60.27	60.07	59.86	59.66
67	62.22	62.01	61.79	61.60	61.38	61.18	60.98	60.77	60.57
68	63.15	62.93	62.72	62.51	62.30	62.10	61.89	61.68	61.47
69	64.08	63.86	63.64	63.43	63.22	63.01	62.80	62.58	62.38
70	65.00	64.79	64.57	64.35	64.13	63.92	63.71	63.49	63.28
71	65.93	65.71	65.49	65.27	65.05	64.83	64.62	64.40	64.18
72	66.86	66.64	66.42	66.19	65.96	65.75	65.53	65.30	65.09
73	67.79	67.57	67.34	67.11	66.88	66.66	66.44	66.21	65.99
74	68.61	68.49	68.26	68.03	67.80	67.57	67.35	67.12	66.90
75	69.64	69.42	69.18	68.95	68.71	68.49	68.26	68.03	67.80
76	70.57	70.34	70.10	69.87	69.63	69.40	69.17	68.93	68.70
77	71.50	71.27	71.03	70.79	70.54	70.31	70.08	69.84	69.61
78	72.43	72.19	71.95	71.70	71.46	71.22	70.99	70.75	70.51
79	73.36	73.12	72.87	72.62	72.38	72.14	71.90	71.65	71.42
80	74.29	74.04	73.79	73.54	73.30	73.05	72.81	72.56	72.32
81	75.22	74.97	74.71	74.46	74.22	73.96	73.72	73.47	73.22
82	76.15	75.89	75.63	75.38	75.13	74.88	74.63	74.37	74.13
83	77.08	76.82	76.56	76.30	76.05	75.79	75.54	75.28	75.03
84	78.00	77.74	77.48	77.22	76.96	76.70	76.45	76.19	75.94
85	78.93	78.67	78.40	78.14	77.88	77.62	77.36	77.10	76.84
86	79.86	79.59	79.32	79.06	78.80	78.53	78.27	78.00	77.74
87	80.79	80.52	80.25	79.98	79.71	79.44	79.18	78.91	78.65
88	81.72	81.44	81.17	80.90	80.63	80.36	80.09	79.82	79.55
89	82.65	82.37	82.09	81.82	81.55	81.27	81.00	80.72	80.46
90	83.57	83.30	83.02	82.74	82.46	82.18	81.91	81.63	81.36
91	84.50	84.22	83.94	83.66	83.38	83.09	82.82	82.54	82.26
92	85.43	85.15	84.86	84.58	84.29	84.01	83.73	83.44	83.17
93	86.36	86.08	85.79	85.50	85.21	84.92	84.64	84.35	84.07
94	87.28	87.00	86.71	86.42	86.13	85.83	85.55	85.26	84.98
95	88.21	87.93	87.63	87.34	87.04	86.75	86.46	86.17	85.88
96	89.14	88.85	88.55	88.26	87.96	87.66	87.37	87.07	86.78
97	90.07	89.78	89.48	89.18	88.87	88.57	88.28	87.98	87.69
98	91.00	90.70	90.40	90.09	89.79	89.48	89.19	88.89	88.59
99	91.93	91.63	91.32	91.01	90.71	90.40	90.10	89.79	89.50
100	92.86	92.55	92.24	91.93	91.62	91.31	91.01	90.70	90.40

TABLE VII.

Table for reducing the Volume of a Gas to 760 mm. Pressure.

For temperatures between 0° and 12°, deduct 1 mm. from the barometer pressure ;  
 between 13° and 19°, 2 mm ; between 20° and 25°, 3 mm.

700	710	712	714	716	718	720	722	724	726	728
1	0.934	0.937	0.940	0.942	0.945	0.947	0.950	0.953	0.955	0.958
2	1.868	1.874	1.879	1.884	1.890	1.895	1.900	1.905	1.911	1.916
3	2.803	2.810	2.818	2.826	2.834	2.842	2.850	2.858	2.866	2.874
4	3.738	3.747	3.758	3.768	3.779	3.789	3.800	3.810	3.821	3.832
5	4.672	4.685	4.697	4.711	4.724	4.736	4.750	4.763	4.777	4.790
6	5.607	5.621	5.637	5.653	5.669	5.684	5.700	5.716	5.732	5.747
7	6.540	6.558	6.577	6.595	6.614	6.631	6.650	6.668	6.687	6.705
8	7.474	7.494	7.516	7.537	7.558	7.578	7.600	7.621	7.642	7.663
9	8.409	8.431	8.456	8.479	8.503	8.526	8.550	8.573	8.598	8.621
10	9.34	9.37	9.40	9.42	9.45	9.47	9.50	9.53	9.55	9.58
11	10.28	10.31	10.34	10.36	10.39	10.42	10.45	10.48	10.51	10.54
12	11.21	11.24	11.27	11.30	11.34	11.37	11.40	11.43	11.46	11.50
13	12.14	12.18	12.21	12.24	12.28	12.31	12.35	12.38	12.41	12.45
14	13.08	13.12	13.16	13.19	13.23	13.26	13.30	13.34	13.37	13.41
15	14.02	14.06	14.10	14.13	14.17	14.21	14.25	14.29	14.33	14.37
16	14.95	14.99	15.03	15.07	15.11	15.15	15.20	15.24	15.28	15.33
17	15.88	15.93	15.98	16.02	16.06	16.10	16.15	16.19	16.23	16.28
18	16.82	16.87	16.92	16.96	17.01	17.05	17.10	17.15	17.19	17.24
19	17.76	17.81	17.86	17.90	17.95	18.00	18.05	18.10	18.15	18.21
20	18.68	18.74	18.79	18.84	18.90	18.95	19.00	19.05	19.11	19.16
21	19.62	19.68	19.73	19.78	19.84	19.90	19.95	20.00	20.06	20.12
22	20.55	20.61	20.67	20.72	20.78	20.84	20.90	20.96	21.01	21.07
23	21.49	21.55	21.61	21.66	21.73	21.79	21.85	21.91	21.97	22.03
24	22.43	22.49	22.55	22.61	22.68	22.74	22.80	22.86	22.92	22.99
25	23.35	23.42	23.49	23.55	23.62	23.69	23.75	23.81	23.88	23.95
26	24.29	24.36	24.43	24.50	24.57	24.64	24.70	24.77	24.83	24.90
27	25.23	25.30	25.37	25.44	25.51	25.58	25.65	25.72	25.79	25.86
28	26.16	26.23	26.30	26.37	26.45	26.53	26.60	26.67	26.74	26.82
29	27.10	27.17	27.24	27.31	27.40	27.48	27.55	27.62	27.70	26.78
30	28.03	28.10	28.18	28.26	28.34	28.42	28.50	28.58	28.66	28.74
31	28.97	29.04	29.12	29.20	29.29	29.37	29.45	29.53	29.62	29.70
32	29.90	29.98	30.06	30.14	30.23	30.32	30.40	30.48	30.57	30.66
33	30.83	30.91	31.00	31.08	31.17	31.26	31.35	31.43	31.52	31.61
34	31.77	31.85	31.94	32.03	32.12	32.21	32.30	32.39	32.48	32.57
35	32.71	32.79	32.88	32.97	33.07	33.16	33.25	33.34	33.44	33.53
36	33.64	33.73	33.82	33.91	34.01	34.10	34.20	34.29	34.39	34.49
37	34.57	34.66	34.76	34.86	34.96	35.05	35.15	35.25	35.35	35.45
38	35.50	35.60	35.70	35.80	35.90	36.00	36.10	36.20	36.30	36.40
39	36.44	36.54	36.64	36.74	36.85	36.95	37.05	37.15	37.26	37.37
40	37.38	37.48	37.58	37.68	37.79	37.89	38.00	38.10	38.21	38.32
41	38.31	38.41	38.52	38.62	38.74	38.84	38.95	39.05	39.17	39.28
42	39.23	39.35	39.46	39.57	39.69	39.79	39.90	40.01	40.12	40.23
43	40.18	40.29	40.40	40.51	40.62	40.73	40.85	40.96	41.08	41.19
44	41.11	41.22	41.34	41.44	41.56	41.68	41.80	41.91	42.03	42.16
45	42.05	42.16	42.28	42.39	42.52	42.63	42.75	42.87	42.99	43.11
46	42.98	43.10	43.22	43.34	43.46	43.58	43.70	43.82	43.94	44.06
47	43.91	44.03	44.15	44.27	44.40	44.52	44.65	44.77	44.90	45.03
48	44.84	44.96	45.09	45.22	45.35	45.47	45.60	45.72	45.85	45.98
49	45.78	45.91	46.04	46.17	46.30	46.42	46.55	46.67	46.80	46.94
50	46.72	46.85	46.97	47.11	47.24	47.36	47.50	47.63	47.77	47.90

Table for reducing the Volume of a Gas, etc.—Continued.

760	710	712	714	716	718	720	722	724	726	728
51	47.65	47.79	47.92	48.05	48.18	48.31	48.45	48.59	48.73	48.86
52	48.58	48.72	48.85	48.99	49.13	49.26	49.40	49.54	49.68	49.82
53	49.52	49.66	49.79	49.93	50.07	50.21	50.35	50.48	50.64	50.78
54	50.45	50.59	50.73	50.87	51.01	51.15	51.30	51.44	51.59	51.73
55	51.38	51.53	51.67	51.82	51.96	52.10	52.25	52.39	52.54	52.69
56	52.32	52.47	52.61	52.76	52.91	53.05	53.20	53.35	53.50	53.65
57	53.25	53.41	53.55	53.70	53.85	54.00	54.15	54.30	54.45	54.60
58	54.19	54.34	54.49	54.64	54.79	54.94	55.10	55.25	55.41	55.56
59	55.13	55.28	55.43	55.59	55.74	55.89	56.05	56.21	56.37	56.52
60	56.07	56.22	56.37	56.53	56.69	56.84	57.00	57.16	57.32	57.47
61	57.00	57.15	57.31	57.47	57.63	57.79	57.95	58.11	58.27	58.43
62	57.93	58.09	58.25	58.41	58.58	58.74	58.90	59.06	59.23	59.39
63	58.87	59.03	59.19	59.35	59.52	59.68	59.85	60.01	60.18	60.35
64	59.80	59.96	60.13	60.30	60.47	60.63	60.80	60.97	61.14	61.30
65	60.74	60.90	61.07	61.24	61.41	61.58	61.75	61.92	62.09	62.26
66	61.67	61.84	62.01	62.18	62.35	62.52	62.70	62.87	63.05	63.22
67	62.60	62.77	62.95	63.12	63.30	63.47	63.65	63.82	64.00	64.18
68	63.54	63.71	63.89	64.06	64.24	64.42	64.60	64.78	64.96	65.13
69	64.47	64.65	64.83	65.01	65.19	65.37	65.55	65.73	65.91	66.09
70	65.40	65.58	65.77	65.95	66.14	66.32	66.50	66.68	66.87	67.05
71	66.34	66.52	66.71	66.89	67.08	67.26	67.45	67.63	67.82	68.01
72	67.27	67.46	67.65	67.83	68.02	68.21	68.40	68.59	68.78	68.97
73	68.20	68.39	68.58	68.77	68.97	69.16	69.35	69.54	69.73	69.92
74	69.14	69.33	69.53	69.72	69.92	70.11	70.30	70.49	70.69	70.88
75	70.07	70.27	70.47	70.66	70.86	71.05	71.25	71.44	71.64	71.84
76	71.01	71.21	71.41	71.60	71.80	72.00	72.20	72.40	72.60	72.80
77	71.94	72.14	72.34	72.54	72.75	72.95	73.15	73.35	73.55	73.75
78	72.87	73.07	73.28	73.48	73.69	73.89	74.10	74.30	74.51	74.71
79	73.80	74.01	74.22	74.42	74.63	74.84	75.05	75.25	75.46	75.67
80	74.74	74.94	75.16	75.37	75.58	75.78	76.00	76.21	76.42	76.63
81	75.67	75.88	76.10	76.31	76.53	76.74	76.95	77.16	77.37	77.58
82	76.60	76.82	77.04	77.25	77.47	77.68	77.90	78.11	78.33	78.54
83	77.54	77.76	77.98	78.19	78.41	78.63	78.85	79.07	79.28	79.50
84	78.47	78.69	78.91	79.13	79.35	79.57	79.80	80.02	80.24	80.46
85	79.41	79.63	79.86	80.08	80.31	80.53	80.75	80.97	81.19	81.41
86	80.34	80.57	80.80	81.02	81.25	81.47	81.70	81.92	82.15	82.37
87	81.28	81.50	81.74	81.96	82.19	82.42	82.65	82.87	83.10	83.33
88	82.21	82.44	82.68	82.90	83.13	83.36	83.60	83.83	84.06	84.29
89	83.15	83.38	83.62	83.85	84.08	84.31	84.55	84.78	85.02	85.25
90	84.09	84.31	84.56	84.79	85.03	85.26	85.50	85.73	85.98	86.21
91	85.02	85.25	85.50	85.73	85.98	86.21	86.45	86.69	86.93	87.17
92	85.95	86.19	86.44	86.68	86.92	87.16	87.40	87.64	87.89	88.13
93	86.89	87.12	87.38	87.62	87.87	88.11	88.35	88.59	88.84	89.08
94	87.82	88.06	88.32	88.56	88.81	89.05	89.30	89.54	89.80	90.04
95	88.76	89.01	89.26	89.50	89.75	90.00	90.25	90.50	90.75	91.00
96	89.69	89.94	90.20	90.45	90.70	90.95	91.20	91.45	91.70	91.95
97	90.62	90.87	91.13	91.38	91.64	91.89	92.15	92.40	92.66	92.91
98	91.56	91.82	92.07	92.33	92.59	92.84	93.10	93.35	93.62	93.87
99	92.49	92.75	93.01	93.26	93.53	93.79	94.05	94.31	94.57	94.83
100	93.42	93.68	93.95	94.21	94.47	94.74	95.00	95.26	95.53	95.79

Table for reducing the Volume of a Gas, etc.—Continued.

760	730	732	734	736	738	740	742	744	746	748
1	0.961	0.963	0.966	0.968	0.971	0.974	0.976	0.979	0.982	0.984
2	1.921	1.926	1.932	1.937	1.942	1.947	1.953	1.958	1.963	1.968
3	2.882	2.889	2.898	2.905	2.913	2.921	2.929	2.937	2.945	2.953
4	3.812	3.852	3.864	3.874	3.884	3.895	3.905	3.916	3.926	3.937
5	4.803	4.816	4.830	4.842	4.855	4.868	4.882	4.895	4.908	4.921
6	5.763	5.778	5.796	5.810	5.826	5.842	5.858	5.874	5.890	5.905
7	6.724	6.742	6.762	6.779	6.797	6.816	6.834	6.853	6.871	6.889
8	7.684	7.705	7.728	7.747	7.768	7.790	7.810	7.832	7.853	7.874
9	8.645	8.668	8.693	8.716	8.739	8.763	8.787	8.811	8.834	8.858
10	9.61	9.63	9.66	9.68	9.71	9.74	9.76	9.79	9.82	9.84
11	10.57	10.59	10.62	10.65	10.68	10.71	10.74	10.77	10.80	10.82
12	11.53	11.56	11.59	11.62	11.65	11.68	11.71	11.75	11.78	11.81
13	12.49	12.52	12.55	12.59	12.62	12.66	12.69	12.73	12.76	12.79
14	13.45	13.48	13.52	13.56	13.59	13.63	13.66	13.70	13.74	13.78
15	14.41	14.44	14.48	14.52	14.56	14.60	14.64	14.69	14.73	14.77
16	15.37	15.41	15.45	15.49	15.53	15.58	15.62	15.67	15.71	15.75
17	16.33	16.37	16.41	16.46	16.50	16.55	16.60	16.65	16.69	16.73
18	17.29	17.33	17.38	17.43	17.47	17.52	17.57	17.62	17.67	17.72
19	18.25	18.29	18.35	18.40	18.45	18.50	18.55	18.60	18.65	18.70
20	19.21	19.26	19.32	19.37	19.42	19.47	19.53	19.58	19.63	19.68
21	20.17	20.22	20.28	20.34	20.39	20.44	20.50	20.56	20.61	20.66
22	21.13	21.19	21.25	21.31	21.36	21.42	21.48	21.54	21.59	21.65
23	22.09	22.15	22.21	22.27	22.33	22.39	22.45	22.51	22.57	22.64
24	23.05	23.11	23.18	23.24	23.30	23.36	23.43	23.50	23.56	23.63
25	24.01	24.07	24.14	24.21	24.27	24.34	24.41	24.48	24.54	24.61
26	24.97	25.04	25.11	25.18	25.24	25.31	25.38	25.45	25.52	25.59
27	25.93	26.00	26.07	26.14	26.21	26.28	26.36	26.43	26.50	26.58
28	26.89	26.96	27.04	27.12	27.18	27.26	27.33	27.41	27.48	27.56
29	27.85	27.92	28.00	28.08	28.15	28.23	28.31	28.39	28.47	28.55
30	28.82	28.89	28.97	29.05	29.13	29.21	29.29	29.37	29.45	29.53
31	29.78	29.86	29.94	30.02	30.10	30.18	30.26	30.35	30.43	30.51
32	30.74	30.82	30.91	30.99	31.07	31.15	31.24	31.33	31.41	31.50
33	31.71	31.78	31.87	31.96	32.04	32.13	32.21	32.30	32.39	32.48
34	32.66	32.75	32.84	32.93	33.01	33.10	33.19	33.28	33.37	33.46
35	33.62	33.71	33.80	33.89	33.98	34.07	34.17	34.27	34.36	34.45
36	34.58	34.67	34.77	34.86	34.95	35.05	35.15	35.25	35.34	35.43
37	35.54	35.63	35.73	35.83	35.92	36.02	36.12	36.22	36.32	36.42
38	36.50	36.60	36.70	36.80	36.90	37.00	37.10	37.20	37.30	37.40
39	37.47	37.57	37.67	37.77	37.87	37.97	38.07	38.18	38.28	38.39
40	38.42	38.52	38.61	38.71	38.81	38.91	39.01	39.11	39.21	39.31
41	39.38	39.48	39.58	39.68	39.78	39.88	40.02	40.14	40.24	40.36
42	40.34	40.44	40.56	40.68	40.78	40.89	41.00	41.12	41.22	41.34
43	41.30	41.46	41.53	41.64	41.75	41.86	41.97	42.10	42.20	42.32
44	42.27	42.38	42.50	42.62	42.73	42.84	42.95	43.07	43.18	43.30
45	43.22	43.34	43.46	43.58	43.69	43.81	43.93	44.06	44.17	44.29
46	44.18	44.30	44.42	44.54	44.66	44.78	44.90	45.03	45.15	45.27
47	45.15	45.28	45.39	45.52	45.64	45.76	45.88	46.01	46.13	46.26
48	46.10	46.23	46.36	46.49	46.61	46.73	46.85	46.99	47.12	47.24
49	47.06	47.19	47.32	47.44	47.57	47.70	47.83	47.97	48.10	48.23
50	48.03	48.18	48.30	48.42	48.55	48.68	48.82	48.95	49.08	49.21



Table for reducing the Volume of a Gas, etc.—*Continued.*

700	730	732	734	736	738	740	742	744	746	748
51	48.99	49.12	49.26	49.39	49.52	49.65	49.79	49.93	50.06	50.19
52	49.96	50.08	50.22	50.36	50.49	50.63	50.77	50.91	51.04	51.18
53	50.91	51.05	51.19	51.33	51.46	51.60	51.75	51.89	52.02	52.16
54	51.87	52.01	52.16	52.30	52.44	52.58	52.72	52.87	53.01	53.15
55	52.83	52.98	53.13	53.27	53.41	53.55	53.70	53.85	53.99	54.14
56	53.79	53.94	54.09	54.23	54.37	54.52	54.68	54.83	54.97	55.11
57	54.75	54.90	55.05	55.20	55.35	55.50	55.65	55.80	55.95	56.10
58	55.71	55.86	56.02	56.17	56.32	56.47	56.63	56.78	56.93	57.08
59	56.67	56.83	56.99	57.14	57.29	57.44	57.60	57.76	57.92	58.07
60	57.63	57.79	57.95	58.10	58.26	58.42	58.58	58.74	58.90	59.05
61	58.59	58.75	58.91	59.07	59.23	59.39	59.56	59.72	59.88	60.04
62	59.55	59.72	59.88	60.04	60.20	60.36	60.53	60.70	60.86	61.02
63	60.51	60.68	60.85	61.01	61.17	61.34	61.51	61.68	61.84	62.00
64	61.47	61.64	61.81	61.98	62.15	62.32	62.49	62.66	62.82	62.99
65	62.43	62.60	62.77	62.94	63.11	63.28	63.46	63.64	63.81	63.98
66	63.39	63.57	63.74	63.91	64.08	64.26	64.44	64.62	64.79	64.96
67	64.35	64.53	64.71	64.88	65.05	65.23	65.41	65.59	65.77	65.94
68	65.31	65.50	65.68	65.85	66.02	66.20	66.38	66.56	66.74	66.92
69	66.27	66.45	66.64	66.82	67.00	67.18	67.37	67.55	67.73	67.91
70	67.24	67.42	67.61	67.79	67.97	68.16	68.34	68.53	68.71	68.89
71	68.20	68.39	68.58	68.76	68.94	69.13	69.32	69.51	69.69	69.88
72	69.16	69.35	69.54	69.73	69.92	70.11	70.30	70.49	70.68	70.86
73	70.12	70.31	70.51	70.69	70.88	71.08	71.27	71.47	71.66	71.85
74	71.08	71.28	71.48	71.66	71.85	72.05	72.25	72.45	72.64	72.83
75	72.04	72.24	72.44	72.63	72.82	73.02	73.22	73.42	73.62	73.82
76	73.00	73.20	73.40	73.60	73.80	74.00	74.20	74.40	74.60	74.80
77	73.96	74.17	74.37	74.57	74.77	74.97	75.18	75.39	75.59	75.79
78	74.92	75.12	75.33	75.53	75.74	75.95	76.16	76.37	76.57	76.77
79	75.88	76.09	76.30	76.50	76.71	76.92	77.13	77.34	77.55	77.75
80	76.84	77.05	77.27	77.47	77.68	77.90	78.10	78.32	78.53	78.74
81	77.80	78.02	78.23	78.44	78.65	78.87	79.08	79.30	79.51	79.72
82	78.76	78.98	79.20	79.41	79.62	79.84	80.06	80.28	80.50	80.71
83	79.72	79.94	80.16	80.38	80.60	80.82	81.04	81.26	81.48	81.69
84	80.68	80.90	81.12	81.34	81.56	81.79	82.01	82.24	82.46	82.68
85	81.64	81.87	82.10	82.31	82.53	82.76	82.99	83.22	83.44	83.66
86	82.60	82.83	83.06	83.28	83.50	83.73	83.97	84.20	84.42	84.64
87	83.56	83.79	84.02	84.25	84.48	84.71	84.94	85.17	85.40	85.62
88	84.52	84.76	85.00	85.22	85.45	85.68	85.92	86.15	86.38	86.61
89	85.48	85.72	85.96	86.19	86.42	86.66	86.89	87.13	87.36	87.59
90	86.45	86.68	86.93	87.16	87.39	87.63	87.87	88.11	88.34	88.58
91	87.41	87.65	87.89	88.12	88.36	88.61	88.85	89.09	89.33	89.56
92	88.37	88.61	88.86	89.09	89.33	89.58	89.82	90.07	90.31	90.55
93	89.33	89.57	89.82	90.06	90.30	90.55	90.80	91.05	91.29	91.53
94	90.29	90.54	90.79	91.03	91.27	91.53	91.78	92.03	92.27	92.51
95	91.25	91.50	91.75	92.00	92.25	92.50	92.75	93.00	93.25	93.50
96	92.21	92.46	92.72	92.97	93.22	93.47	93.73	93.98	94.23	94.48
97	93.17	93.43	93.68	93.93	94.19	94.45	94.71	94.96	95.22	95.47
98	94.13	94.39	94.65	94.90	95.16	95.42	95.68	95.94	96.20	96.45
99	95.09	95.35	95.61	95.87	96.13	96.39	96.66	96.92	97.18	97.43
100	96.05	96.32	96.58	96.84	97.11	97.37	97.63	97.89	98.16	98.42

Table for reducing the Volume of a Gas, etc.—Continued.

760	750	752	754	756	758	762	764	766	768	770
1	0.987	0.989	0.992	0.995	0.997	1.003	1.005	1.008	1.011	1.013
2	1.974	1.979	1.984	1.989	1.995	2.005	2.011	2.016	2.021	2.026
3	2.960	2.968	2.976	2.984	2.992	3.007	3.016	3.024	3.032	3.039
4	3.947	3.958	3.968	3.979	3.990	4.010	4.021	4.032	4.042	4.052
5	4.934	4.947	4.960	4.974	4.987	5.013	5.026	5.040	5.053	5.066
6	5.921	5.937	5.952	5.968	5.984	6.016	6.032	6.047	6.063	6.079
7	6.908	6.926	6.944	6.963	6.982	7.018	7.037	7.055	7.074	7.092
8	7.894	7.916	7.936	7.958	7.979	8.021	8.042	8.063	8.084	8.106
9	8.881	8.905	8.929	8.952	8.977	9.023	9.048	9.071	9.095	9.119
10	9.87	9.89	9.92	9.95	9.97	10.03	10.05	10.08	10.11	10.13
11	10.85	10.88	10.91	10.94	10.97	11.03	11.06	11.09	11.12	11.14
12	11.84	11.87	11.90	11.94	11.97	12.04	12.07	12.10	12.13	12.16
13	12.83	12.86	12.89	12.93	12.96	13.04	13.07	13.10	13.14	13.17
14	13.82	13.85	13.88	13.92	13.96	14.04	14.07	14.11	14.15	14.17
15	14.81	14.84	14.87	14.92	14.96	15.04	15.08	15.12	15.16	15.19
16	15.79	15.83	15.87	15.91	15.95	16.05	16.09	16.13	16.17	16.21
17	16.78	16.82	16.86	16.91	16.95	17.05	17.09	17.14	17.18	17.22
18	17.77	17.81	17.85	17.90	17.95	18.05	18.10	18.15	18.19	18.23
19	18.75	18.80	18.85	18.90	18.95	19.05	19.10	19.15	19.20	19.25
20	19.74	19.79	19.84	19.89	19.95	20.05	20.11	20.16	20.21	20.26
21	20.72	20.77	20.83	20.89	20.94	21.05	21.11	21.17	21.22	21.27
22	21.71	21.76	21.82	21.88	21.94	22.06	22.12	22.18	22.23	22.28
23	22.70	22.75	22.81	22.88	22.94	23.06	23.12	23.18	23.24	23.30
24	23.69	23.74	23.80	23.87	23.93	24.06	24.13	24.19	24.25	24.31
25	24.67	24.73	24.80	24.87	24.93	25.06	25.13	25.20	25.26	25.32
26	25.66	25.72	25.79	25.86	25.93	26.06	26.14	26.21	26.27	26.34
27	26.65	26.71	26.78	26.86	26.93	27.07	27.15	27.22	27.28	27.35
28	27.63	27.70	27.77	27.85	27.92	28.07	28.15	28.23	28.29	28.36
29	28.62	28.69	28.76	28.84	28.92	29.07	29.16	29.24	29.30	29.37
30	29.60	29.68	29.76	29.84	29.92	30.07	30.16	30.24	30.32	30.39
31	30.59	30.67	30.75	30.84	30.92	31.08	31.17	31.25	31.33	31.41
32	31.58	31.66	31.74	31.83	31.92	32.08	32.17	32.26	32.34	32.42
33	32.56	32.65	32.73	32.82	32.91	33.08	33.18	33.27	33.35	33.43
34	33.55	33.64	33.73	33.82	33.91	34.09	34.18	34.28	34.36	34.45
35	34.54	34.63	34.72	34.82	34.91	35.09	35.19	35.28	35.37	35.46
36	35.52	35.62	35.71	35.81	35.91	36.09	36.19	36.29	36.38	36.47
37	36.51	36.61	36.71	36.81	36.90	37.09	37.20	37.30	37.39	37.49
38	37.50	37.60	37.70	37.80	37.90	38.10	38.20	38.30	38.40	38.50
39	38.49	38.59	38.69	38.80	38.90	39.10	39.21	39.31	39.41	39.51
40	39.47	39.58	39.68	39.79	39.90	40.10	40.21	40.32	40.42	40.52
41	40.46	40.56	40.67	40.79	40.89	41.11	41.22	41.33	41.43	41.54
42	41.44	41.55	41.66	41.78	41.89	42.11	42.22	42.34	42.44	42.55
43	42.43	42.54	42.66	42.78	42.89	43.11	43.23	43.35	43.45	43.56
44	43.42	43.53	43.65	43.77	43.89	44.12	44.23	44.35	44.46	44.58
45	44.40	44.52	44.64	44.76	44.88	45.12	45.24	45.36	45.47	45.59
46	45.39	45.51	45.63	45.76	45.88	46.12	46.24	46.36	46.48	46.60
47	46.38	46.50	46.63	46.76	46.88	47.12	47.25	47.38	47.49	47.61
48	47.36	47.49	47.62	47.75	47.87	48.13	48.25	48.39	48.51	48.63
49	48.35	48.48	48.61	48.74	48.87	49.13	49.26	49.40	49.52	49.64
50	49.34	49.47	49.60	49.74	49.87	50.13	50.26	50.40	50.53	50.66

Table for reducing the Volume of a Gas, etc.—Continued.

760	750	752	754	756	758	762	764	766	768	770
51	50.33	50.46	50.60	50.74	50.87	51.14	51.27	51.41	51.54	51.67
52	51.32	51.45	51.59	51.73	51.87	52.14	52.28	52.42	52.55	52.68
53	52.30	52.44	52.58	52.72	52.87	53.14	53.28	53.42	53.56	53.70
54	53.29	53.43	53.57	53.72	53.86	54.14	54.28	54.43	54.57	54.72
55	54.28	54.42	54.56	54.71	54.86	55.15	55.29	55.44	55.58	55.73
56	55.26	55.41	55.56	55.71	55.86	56.15	56.29	56.44	56.59	56.74
57	56.25	56.40	56.55	56.70	56.85	57.15	57.30	57.45	57.60	57.76
58	57.24	57.39	57.54	57.69	57.85	58.15	58.30	58.46	58.61	58.77
59	58.22	58.38	58.53	58.69	58.85	59.16	59.31	59.47	59.62	59.78
60	59.21	59.37	59.52	59.68	59.84	60.16	60.32	60.47	60.63	60.79
61	60.20	60.36	60.52	60.68	60.84	61.16	61.32	61.48	61.64	61.81
62	61.19	61.35	61.51	61.67	61.84	62.16	62.33	62.49	62.65	62.82
63	62.17	62.34	62.50	62.67	62.83	63.17	63.33	63.50	63.67	63.84
64	63.16	63.33	63.49	63.66	63.83	64.17	64.34	64.51	64.68	64.85
65	64.15	64.32	64.49	64.66	64.83	65.17	65.34	65.51	65.69	65.86
66	65.13	65.31	65.48	65.65	65.82	66.17	66.35	66.52	66.70	66.88
67	66.12	66.30	66.47	66.64	66.82	67.18	67.35	67.53	67.71	67.89
68	67.10	67.29	67.46	67.64	67.82	68.18	68.36	68.54	68.72	68.90
69	68.09	68.28	68.45	68.63	68.82	69.18	69.36	69.54	69.73	69.91
70	69.08	69.26	69.44	69.63	69.82	70.18	70.37	70.55	70.74	70.92
71	70.07	70.25	70.43	70.62	70.81	71.19	71.37	71.56	71.75	71.94
72	71.05	71.24	71.43	71.62	71.81	72.19	72.38	72.57	72.76	72.95
73	72.04	72.23	72.42	72.61	72.81	73.19	73.38	73.57	73.77	73.97
74	73.03	73.22	73.41	73.61	73.80	74.19	74.39	74.58	74.78	74.98
75	74.01	74.21	74.40	74.60	74.80	75.20	75.39	75.59	75.79	75.99
76	75.00	75.20	75.40	75.60	75.80	76.20	76.40	76.60	76.80	77.01
77	75.99	76.19	76.39	76.59	76.79	77.20	77.40	77.60	77.81	78.02
78	76.97	77.18	77.38	77.58	77.79	78.20	78.41	78.61	78.82	79.03
79	77.96	78.17	78.37	78.58	78.79	79.21	79.41	79.62	79.83	80.04
80	78.94	79.16	79.36	79.58	79.79	80.21	80.42	80.63	80.84	81.06
81	79.93	80.15	80.35	80.57	80.79	81.21	81.42	81.64	81.85	82.07
82	80.92	81.14	81.35	81.56	81.78	82.21	82.43	82.65	82.87	83.09
83	81.91	82.13	82.34	82.56	82.78	83.22	83.44	83.66	83.88	84.10
84	82.90	83.12	83.34	83.56	83.78	84.22	84.44	84.66	84.89	85.11
85	83.88	84.11	84.33	84.55	84.78	85.22	85.45	85.67	85.90	86.13
86	84.87	85.10	85.32	85.55	85.78	86.22	86.46	86.67	86.91	87.14
87	85.85	86.08	86.31	86.54	86.77	87.23	87.46	87.68	87.92	88.15
88	86.84	87.07	87.30	87.54	87.77	88.23	88.47	88.69	88.93	89.17
89	87.82	88.06	88.29	88.53	88.77	89.23	89.47	89.70	89.94	90.18
90	88.81	89.05	89.29	89.52	89.77	90.23	90.48	90.71	90.95	91.19
91	89.80	90.04	90.28	90.52	90.76	91.24	91.48	91.72	91.96	92.21
92	90.79	91.03	91.27	91.51	91.76	92.24	92.49	92.73	92.97	93.22
93	91.77	92.02	92.26	92.51	92.76	93.24	93.49	93.74	93.98	94.23
94	92.76	93.01	93.26	93.50	93.75	94.24	94.49	94.74	94.99	95.24
95	93.74	94.00	94.25	94.50	94.75	95.25	95.50	95.75	96.00	96.26
96	94.73	94.98	95.24	95.49	95.75	96.25	96.51	96.76	97.01	97.27
97	95.72	95.97	96.23	96.49	96.75	97.25	97.51	97.77	98.02	98.28
98	96.70	96.96	97.22	97.48	97.74	98.25	98.52	98.77	99.03	99.30
99	97.69	97.95	98.21	98.48	98.74	99.26	99.52	99.78	100.04	100.31
100	98.68	98.95	99.21	99.47	99.74	100.26	100.53	100.79	101.05	101.32

TABLE VIII.

Table of the Tension of Water Vapour between  $-20^{\circ}$  and  
 $+118^{\circ}$  C. in mm. of Mercury. Magnus.

T.	Mm.	T.	Mm.	T.	Mm.	T.	Mm.
$-20^{\circ}$	0.916	$+15^{\circ}$	12.677	$+50^{\circ}$	92.0	$+85^{\circ}$	432.3
19	0.999	16	13.519	51	96.6	86	449.6
18	1.039	17	14.409	52	101.5	87	467.5
17	1.186	18	15.351	53	106.6	88	486.0
16	1.290	19	16.345	54	111.9	89	505.0
15	1.403	20	17.396	55	117.4	90	524.8
14	1.525	21	18.505	56	123.1	91	545.1
13	1.655	22	19.675	57	129.1	92	566.1
12	1.796	23	20.909	58	135.3	93	587.8
11	1.947	24	22.211	59	141.8	94	610.2
10	2.109	25	23.582	60	148.6	95	633.3
9	2.284	26	25.026	61	155.6	96	657.1
8	2.471	27	26.547	62	162.9	97	681.7
7	2.671	28	28.148	63	170.5	98	707.0
6	2.886	29	29.832	64	178.4	99	733.1
5	3.110	30	31.602	65	186.6	100	760.0
4	3.361	31	33.5	66	195.1	101	787.7
3	3.624	32	35.4	67	204.0	102	816.3
2	3.900	33	37.5	68	213.2	103	845.7
1	4.205	34	39.6	69	222.7	104	876.0
0	4.525	35	41.9	70	232.6	105	907.1
$+1$	4.867	36	44.3	71	242.9	106	939.2
2	5.231	37	46.8	72	253.5	107	972.3
3	5.619	38	49.4	73	264.6	108	1006.3
4	6.032	39	52.1	74	276.0	109	1041.3
5	6.471	40	55.0	75	287.9	110	1077.3
6	6.939	41	58.0	76	300.2	111	1114.3
7	7.436	42	61.1	77	312.9	112	1152.3
8	7.964	43	64.4	78	326.1	113	1191.4
9	8.525	44	67.8	79	339.8	114	1231.7
10	9.126	45	71.4	80	353.9	115	1273.0
11	9.756	46	75.2	81	368.6	116	1315.5
12	10.421	47	79.1	82	383.7	117	1359.1
13	11.130	48	83.2	83	399.4	118	1403.9
14	11.882	49	87.5	84	415.6		

TABLE IX. (*Text, p. 146.*)

Table for the Conversion of Volumes of Gas, obtained in the Gas-Volumeter, into Weights of Active Constituents.

1	2	3	4	5
Substance Analysed.	Active Constituent.	Method of Analysis.	Gas Evolved.	1 c.c. Gas = Active Constituent in mg.
Organic substances	Nitrogen	Dumas' method	N <sub>2</sub>	1.2505
Ammonium salts	Do.	{ With sodium } hypobromite	N <sub>2</sub>	1.2818 <sup>1</sup>
Do.	Ammonia	Do.	N <sub>2</sub>	1.5582 <sup>1</sup>
Urine	Urea	Do.	N <sub>2</sub>	2.956 <sup>1</sup>
Bone-charcoal, marl, etc.	Carbon dioxide	{ Decomposition } by HCl	CO <sub>2</sub>	1.976
Do.	Calcium carbonate	Do.	CO <sub>2</sub>	4.497
Pyrolusite	Manganese dioxide	With H <sub>2</sub> O <sub>2</sub>	O <sub>2</sub>	3.885
Bleaching powder	Chlorine	Do.	O <sub>2</sub>	1.6095
Potassium permanganate	Oxygen	Do.	O <sub>2</sub>	0.7146
Chili saltpetre	Sodium nitrate	In nitrometer	NO	3.7686
Nitrous vitriol	N <sub>2</sub> O <sub>3</sub>	Do.	NO	1.6975
Do.	HNO <sub>3</sub>	Do.	NO	2.8144
Do.	{ Nitric acid of sp. } gr. 1.33	Do.	NO	5.3771
Do.	Sodium nitrate	Do.	NO	3.7986
Nitroglycerine, dynamite, etc.	Trinitroglycerine	Do.	NO	3.358
Do.	Nitrogen	Do.	NO	0.6257
Nitrocellulose, pyroxylin	Do.	Do.	NO	0.6257

<sup>1</sup> These values are corrected for the "nitrogen absorption"; 2.5 per cent. in the case of ammonium salts, and 9 per cent. in the case of urea. (*Cf. p. 131.*)

TABLE X. (*Text*, p. 159.)

Comparison of various Baumé Hydrometers, for Heavy Liquids  
with Specific Gravities.

Degrees.	Rational Hydrometer. $d = \frac{144.3}{144.3 - n.}$	Baumé's Hydrometer according to Gerlach's Scale.	American Scale. $d = \frac{145}{145 - n.}$	Degrees.	Rational Hydrometer. $d = \frac{144.3}{144.3 - n.}$	Baumé's Hydrometer according to Gerlach's Scale.	American Scale. $d = \frac{145}{145 - n.}$
1	1.007	1.0068	1.005	34	1.308	1.3015	1.309
2	1.014	1.0138	1.011	35	1.320	1.3131	1.317
3	1.022	1.0208	1.023	36	1.332	1.3250	1.334
4	1.029	1.0280	1.029	37	1.345	1.3370	1.342
5	1.037	1.0353	1.036	38	1.357	1.3494	1.359
6	1.045	1.0426	1.043	39	1.370	1.3619	1.368
7	1.052	1.0501	1.050	40	1.383	1.3746	1.386
8	1.060	1.0576	1.057	41	1.397	1.3876	1.395
9	1.067	1.0653	1.064	42	1.410	1.4009	1.413
10	1.075	1.0731	1.071	43	1.424	1.4134	1.422
11	1.083	1.0810	1.086	44	1.438	1.4281	1.441
12	1.091	1.0890	1.093	45	1.453	1.4421	1.451
13	1.100	1.0972	1.100	46	1.468	1.4564	1.470
14	1.108	1.1054	1.107	47	1.483	1.4710	1.480
15	1.116	1.1138	1.114	48	1.498	1.4860	1.500
16	1.125	1.1224	1.122	49	1.514	1.5012	1.510
17	1.134	1.1310	1.136	50	1.530	1.5167	1.531
18	1.142	1.1398	1.143	51	1.540	1.5325	1.541
19	1.152	1.1487	1.150	52	1.563	1.5487	1.561
20	1.162	1.1578	1.158	53	1.580	1.5652	1.573
21	1.171	1.1670	1.172	54	1.597	1.5820	1.594
22	1.180	1.1763	1.179	55	1.615	1.5993	1.616
23	1.190	1.1858	1.186	56	1.634	1.6169	1.627
24	1.200	1.1955	1.201	57	1.652	1.6349	1.650
25	1.210	1.2053	1.208	58	1.671	1.6533	1.661
26	1.220	1.2153	1.216	59	1.691	1.6721	1.683
27	1.231	1.2254	1.231	60	1.711	1.6914	1.705
28	1.241	1.2357	1.238	61	1.732	1.7111	1.727
29	1.252	1.2462	1.254	62	1.753	1.7313	1.747
30	1.263	1.2569	1.262	63	1.774	1.7520	1.767
31	1.274	1.2677	1.269	64	1.796	1.7731	1.793
32	1.285	1.2788	1.285	65	1.819	1.7948	1.814
33	1.297	1.2901	1.293	66	1.842	1.8171	1.835

TABLE XI. (*Text*, p. 160.)

Table for the Conversion of Specific Gravities, at  $\frac{15}{4}^{\circ}$ , into  
 "Rational" Baumé degrees.

Sp. gr.	0	1	2	3	4	5	6	7	8	9
0.99	...	...	...	...	...	...	...	...	...	-0.018
1.00	0.126	0.270	0.414	0.557	0.700	0.843	0.986	1.128	1.270	1.412
01	1.553	1.694	1.835	1.976	2.117	2.257	2.397	2.536	2.675	2.814
02	2.953	3.091	3.229	3.367	3.505	3.643	3.780	3.917	4.053	4.189
03	4.325	4.461	4.596	4.731	4.866	5.001	5.135	5.269	5.403	5.537
04	5.671	5.804	5.937	6.070	6.202	6.334	6.466	6.598	6.729	6.860
1.05	6.991	7.122	7.252	7.382	7.512	7.642	7.771	7.900	8.029	8.158
06	8.287	8.415	8.543	8.671	8.798	8.925	9.052	9.179	9.306	9.432
07	9.558	9.684	9.809	9.934	10.059	10.184	10.309	10.433	10.557	10.681
08	10.805	10.929	11.052	11.175	11.298	11.421	11.543	11.665	11.787	11.909
09	12.030	12.151	12.272	12.393	12.514	12.634	12.754	12.874	12.994	13.114
1.10	13.233	13.352	13.471	13.590	13.708	13.826	13.944	14.062	14.179	14.296
11	14.413	14.530	14.647	14.764	14.880	14.996	15.112	15.228	15.343	15.458
12	15.573	15.688	15.803	15.917	16.031	16.145	16.259	16.373	16.486	16.599
13	16.712	16.825	16.938	17.050	17.162	17.274	17.386	17.498	17.610	17.721
14	17.832	17.943	18.054	18.164	18.274	18.384	18.494	18.604	18.713	18.822
1.15	18.931	19.040	19.149	19.258	19.366	19.474	19.582	19.690	19.798	19.905
16	20.012	20.119	20.226	20.333	20.439	20.545	20.651	20.757	20.863	20.969
17	21.074	21.179	21.284	21.389	21.494	21.599	21.703	21.807	21.911	22.015
18	22.119	22.222	22.325	22.428	22.531	22.634	22.737	22.839	22.941	23.043
19	23.145	23.247	23.349	23.450	23.551	23.652	23.753	23.854	23.955	24.055
1.20	24.155	24.255	24.355	24.455	24.554	24.653	24.752	24.851	24.950	25.049
21	25.148	25.246	25.344	25.442	25.540	25.638	25.736	25.834	25.931	26.028
22	26.125	26.222	26.319	26.415	26.511	26.607	26.703	26.799	26.895	26.990
23	27.085	27.180	27.275	27.370	27.465	27.560	27.655	27.749	27.843	27.937
24	28.031	28.125	28.219	28.312	28.405	28.498	28.591	28.684	28.777	28.869
1.25	28.961	29.053	29.145	29.237	29.329	29.420	29.512	29.603	29.694	29.785
26	29.876	29.967	30.058	30.149	30.239	30.329	30.419	30.509	30.599	30.688
27	30.777	30.866	30.955	31.044	31.133	31.222	31.311	31.400	31.488	31.576
28	31.664	31.752	31.840	31.928	32.015	32.102	32.189	32.276	32.363	32.450
29	32.537	32.624	32.711	32.797	32.883	32.969	33.055	33.141	33.227	33.312
1.30	33.397	33.482	33.567	33.652	33.737	33.822	33.907	33.991	34.075	34.159
31	34.243	34.327	34.411	34.495	34.579	34.662	34.745	34.828	34.911	34.994
32	35.077	35.160	35.243	35.325	35.407	35.489	35.571	35.653	35.735	35.817
33	35.899	35.981	36.062	36.143	36.224	36.305	36.386	36.467	36.548	36.628
34	36.708	36.788	36.868	36.948	37.028	37.107	37.187	37.267	37.346	37.425
1.35	37.504	37.583	37.662	37.741	37.820	37.898	37.977	38.056	38.134	38.212
36	38.290	38.368	38.446	38.524	38.601	38.678	38.755	38.832	38.909	38.986
37	39.063	39.140	39.217	39.294	39.370	39.446	39.522	39.598	39.674	39.750
38	39.826	39.902	39.978	40.053	40.128	40.203	40.278	40.353	40.428	40.503
39	40.578	40.653	40.727	40.801	40.875	40.949	41.023	41.097	41.171	41.245

Table for the Conversion of Specific Gravities—Continued.

Sp. gr.	0	1	2	3	4	5	6	7	8	9
140	41318	41392	41466	41539	41612	41685	41758	41831	41904	41977
41	42049	42122	42194	42266	42338	42410	42482	42554	42626	42698
42	42769	42840	42912	42983	43054	43125	43196	43267	43338	43409
43	43479	43550	43620	43690	43760	43830	43900	43970	44040	44110
44	44179	44248	44318	44387	44456	44525	44594	44663	44732	44801
145	44869	44938	45007	45075	45143	45211	45279	45347	45415	45483
45	45551	45619	45687	45754	45821	45888	45955	46022	46089	46156
46	46223	46290	46357	46423	46489	46555	46621	46687	46753	46819
47	46885	46951	47017	47083	47148	47213	47279	47344	47409	47474
48	47539	47604	47669	47734	47799	47863	47928	47992	48056	48120
150	48184	48248	48312	48376	48440	48503	48567	48631	48694	48757
51	48820	48884	48947	49010	49073	49136	49199	49262	49325	49387
52	49449	49512	49574	49636	49698	49760	49822	49884	49946	50008
53	50069	50131	50193	50254	50315	50376	50437	50498	50559	50620
54	50681	50742	50803	50864	50924	50984	51045	51105	51165	51225
155	51285	51345	51405	51465	51525	51584	51643	51703	51763	51822
55	51881	51940	51999	52058	52117	52176	52235	52294	52353	52411
56	52469	52528	52587	52645	52703	52761	52819	52877	52935	52993
57	53051	53109	53167	53225	53282	53339	53397	53454	53511	53568
58	53625	53682	53739	53796	53853	53909	53966	54023	54079	54135
160	54191	54248	54304	54360	54416	54472	54528	54584	54640	54696
61	54751	54807	54863	54918	54973	55028	55083	55138	55193	55248
62	55303	55358	55413	55468	55523	55577	55632	55687	55742	55796
63	55850	55904	55958	56012	56066	56120	56174	56228	56282	56336
64	56389	56443	56497	56550	56603	56656	56709	56763	56816	56869
165	56929	56975	57028	57081	57134	57186	57239	57292	57344	57396
65	57448	57501	57553	57605	57657	57709	57761	57813	57865	57917
66	57968	58020	58072	58124	58175	58226	58278	58329	58380	58431
67	58482	58533	58584	58635	58686	58737	58788	58839	58890	58940
68	58990	59041	59092	59142	59192	59242	59292	59342	59392	59442
170	59492	59542	59592	59641	59691	59741	59791	59840	59890	59939
71	59988	60038	60087	60136	60185	60234	60283	60332	60381	60430
72	60478	60527	60576	60625	60673	60721	60770	60818	60866	60914
73	60962	61010	61058	61106	61154	61202	61250	61298	61346	61394
74	61441	61489	61537	61585	61632	61679	61727	61774	61821	61868
175	61915	61962	62009	62056	62103	62150	62197	62244	62291	62337
75	62383	62430	62477	62523	62569	62615	62662	62708	62754	62800
76	62846	62892	62938	62984	63030	63075	63121	63167	63213	63258
77	63303	63349	63395	63440	63485	63530	63576	63621	63666	63711
78	63756	63801	63846	63891	63936	63980	64025	64070	64115	64159
180	64203	64248	64293	64337	64381	64425	64469	64514	64558	64602
81	64646	64690	64734	64778	64822	64866	64910	64954	64998	65041
82	65084	65128	65172	65215	65258	65301	65345	65388	65431	65474
83	65517	65560	65603	65646	65689	65731	65774	65817	65860	65902
84	65944	65987	66030	66073	66115	66157	66200	66242	66284	66326
185	66368	...	...	...	...	...	...	...	...	...



TABLE XII. (*Text, p. 1*)

Comparison of various Hydrometers, for Liquids lighter than Water, with Specific Gravities.

Degrees. Baumé, Cartier, and Beck.	Baumé.	Cartier.	Beck.	Degrees. Baumé, Cartier, and Beck.	Baumé.	Cartier.	Beck.
	Sp. gr.	Sp. gr.	Sp. gr.		Sp. gr.	Sp. gr.	Sp. gr.
0	...	...	1.0000	36	0.8488	0.8439	0.8252
1	...	...	0.9941	37	0.8439	0.8387	0.8212
2	...	...	0.9883	38	0.8391	0.8336	0.8173
3	...	...	0.9826	39	0.8343	0.8286	0.8133
4	...	...	0.9770	40	0.8295	...	0.8095
5	...	...	0.9714	41	0.8249	...	0.8061
6	...	...	0.9659	42	0.8202	...	0.8018
7	...	...	0.9604	43	0.8156	...	0.7981
8	...	...	0.9550	44	0.8111	...	0.7944
9	...	...	0.9497	45	0.8066	...	0.7907
10	1.0000	...	0.9444	46	0.8022	...	0.7871
11	0.9932	1.0000	0.9392	47	0.7978	...	0.7834
12	0.9865	0.9922	0.9340	48	0.7935	...	0.7799
13	0.9799	0.9846	0.9289	49	0.7892	...	0.7763
14	0.9733	0.9784	0.9239	50	0.7849	...	0.7727
15	0.9669	0.9695	0.9189	51	0.7807	...	0.7692
16	0.9605	0.9627	0.9139	52	0.7766	...	0.7658
17	0.9542	0.9560	0.9090	53	0.7725	...	0.7623
18	0.9480	0.9493	0.9042	54	0.7684	...	0.7589
19	0.9420	0.9427	0.8994	55	0.7643	...	0.7556
20	0.9359	0.9363	0.8947	56	0.7604	...	0.7522
21	0.9299	0.9299	0.8900	57	0.7565	...	0.7489
22	0.9241	0.9237	0.8854	58	0.7526	...	0.7456
23	0.9183	0.9175	0.8808	59	0.7487	...	0.7423
24	0.9125	0.9114	0.8762	60	0.7449	...	0.7391
25	0.9068	0.9054	0.8717	61	...	...	0.7359
26	0.9012	0.8994	0.8673	62	...	...	0.7328
27	0.8957	0.8935	0.8629	63	...	...	0.7296
28	0.8902	0.8877	0.8585	64	...	...	0.7265
29	0.8848	0.8820	0.8542	65	...	...	0.7234
30	0.8795	0.8783	0.8500	66	...	...	0.7203
31	0.8742	0.8707	0.8457	67	...	...	0.7173
32	0.8690	0.8652	0.8415	68	...	...	0.7142
33	0.8639	0.8598	0.8374	69	...	...	0.7112
34	0.8588	0.8545	0.8333	70	...	...	0.7083
35	0.8538	0.8491	0.8292				

TABLE XIII. (*Text*, p. 171.)

Table for the Reduction of the Anemometer Readings to Velocity of Current, expressed in feet per second.

Column *a* gives the anemometer readings in inches; column *b* the velocity in feet per second at a temperature of 15° C.=60° F., and barometric pressure 760 mm.=29.92 inches.

<i>a.</i> Inches.	<i>b.</i> Feet per sec.	<i>a.</i> Inches.	<i>b.</i> Feet per sec.	<i>a.</i> Inches.	<i>b.</i> Feet per sec.	<i>a.</i> Inches.	<i>b.</i> Feet per sec.
·01	2·855	·16	11·42	·32	16·15	·95	27·83
·02	4·038	·17	11·77	·34	16·65	1·00	28·55
·03	4·945	·18	12·11	·36	17·13	1·25	31·93
·04	5·710	·19	12·45	·38	17·60	1·50	34·97
·05	6·384	·20	12·77	·40	18·06	1·75	37·77
·06	6·993	·21	13·08	·45	19·15	2·00	40·37
·07	7·554	·22	13·39	·50	20·18	...	...
·08	8·075	·23	13·70	·55	21·17	...	...
·09	8·565	·24	13·99	·60	22·12	...	...
·10	9·028	·25	14·28	·65	23·02	...	...
·11	9·469	·26	14·56	·70	23·89	...	...
·12	9·891	·27	14·84	·75	24·73	...	...
·13	10·29	·28	15·11	·80	25·54	...	...
·14	10·68	·29	15·38	·85	26·32	...	...
·15	11·06	·30	15·64	·90	27·08	...	...

TABLE XIV. (*Text*, p. 172.)

Table for the Reduction of the Anemometer Readings to Velocity of Current, expressed in metres per second.

Column *a* gives the anemometer readings in millimetres; column *b* the velocity in metres per second at a temperature of 15° C., and barometric pressure 760 mm.

<i>a.</i> mm.	<i>b.</i> m.	<i>a.</i> mm.	<i>b.</i> m.	<i>a.</i> mm.	<i>b.</i> m.	<i>a.</i> mm.	<i>b.</i> m.	<i>a.</i> mm.	<i>b.</i> m.	<i>a.</i> mm.	<i>b.</i> m.
0·1	0·575	1·4	2·040	2·7	2·833	5·0	3·855	10·0	5·452	19·0	7·515
0·2	0·771	1·5	2·111	2·8	2·885	5·2	3·931	10·5	5·586	20·0	7·710
0·3	0·944	1·6	2·181	2·9	2·935	5·4	4·006	11·0	5·718	21	7·900
0·4	1·090	1·7	2·248	3·0	2·986	5·6	4·080	11·5	5·846	22	8·086
0·5	1·205	1·8	2·313	3·2	3·077	5·8	4·152	12·0	5·972	23	8·268
0·6	1·341	1·9	2·376	3·4	3·179	6·0	4·223	12·5	6·095	24	8·446
0·7	1·442	2·0	2·438	3·6	3·271	6·5	4·395	13·0	6·216	25	8·620
0·8	1·560	2·1	2·498	3·8	3·361	7·0	4·561	13·5	6·334	30	9·443
0·9	1·636	2·2	2·557	4·0	3·448	7·5	4·721	14·0	6·450	35	10·199
1·0	1·724	2·3	2·615	4·2	3·569	8·0	4·876	15·0	6·677	40	10·903
1·1	1·808	2·4	2·671	4·4	3·616	8·5	5·026	16·0	6·896	45	11·565
1·2	1·889	2·5	2·728	4·6	3·698	9·0	5·172	17·0	7·108	50	12·190
1·3	1·966	2·6	2·779	4·8	3·777	9·5	5·314	18·0	7·314	...	...

TABLE XV. (*Test, p. 172.*)

Table for Correction for the Temperature at which the Anemometer Readings are made, to 15 C. 60 F.

Column *a* gives the observed temperature; column *b*, the factor by which the values in column *b* of Tables I. and II. must be multiplied, to give the correct velocity.

<i>a.</i> t C.	<i>b.</i>	<i>a.</i> t C.	<i>b.</i>	<i>a.</i> t C.	<i>b.</i>	<i>a.</i> t C.	<i>b.</i>	<i>a.</i> t C.	<i>b.</i>	<i>a.</i> t C.	<i>b.</i>
-10	1.046	18	0.995	42	0.956	66	0.922	140	0.845	260	0.735
-5	1.036	20	0.991	44	0.953	68	0.919	150	0.845	270	0.728
0	1.027	22	0.988	46	0.950	70	0.916	160	0.815	280	0.721
2	1.022	24	0.985	48	0.947	75	0.912	170	0.806	290	0.715
4	1.020	26	0.981	50	0.944	80	0.903	180	0.797	300	0.709
6	1.016	28	0.978	52	0.941	85	0.899	190	0.788	320	0.697
8	1.012	30	0.975	54	0.938	90	0.890	200	0.780	340	0.685
10	1.009	32	0.972	56	0.935	95	0.884	210	0.772	360	0.676
12	1.005	34	0.968	58	0.933	100	0.878	220	0.764	400	0.654
14	1.003	36	0.965	60	0.930	110	0.867	230	0.756	450	0.631
15	1.000	38	0.962	62	0.927	120	0.856	240	0.749	500	0.603
16	0.998	40	0.959	64	0.924	130	0.845	250	0.742	...	...

TABLE XVI. (*Test, p. 176.*)

Table of Temperatures indicated by Seger Cones.

Number of Cone.	Temperature, °C.	Number of Cone.	Temperature, °C.	Number of Cone.	Temperature, °C.	Number of Cone.	Temperature, °C.	Number of Cone.	Temperature, °C.
022	590	010	950	3	1190	15	1430	27	1670
021	620	09	970	4	1210	16	1450	28	1690
020	650	08	990	5	1230	17	1470	29	1710
019	680	07	1010	6	1250	18	1490	30	1730
018	710	06	1030	7	1270	19	1510	31	1750
017	740	05	1050	8	1290	20	1530	32	1770
016	770	04	1070	9	1310	21	1550	33	1790
015	800	03	1090	10	1330	22	1570	34	1810
014	830	02	1110	11	1350	23	1590	35	1830
013	860	01	1130	12	1370	24	1610	36	1850
012	890	1	1150	13	1390	25	1630	...	...
011	920	2	1170	14	1410	26	1650	...	...

Table for Correcting the Volume of Gases having a Calorific Value of 5000 Calories ( $\pm 200$  Calories), per cubic metre, to 15° C. and 760 mm.

The figures give the amount to be added to the ascertained calorific value; the inclined figures are minus values.

Min.	10°	11°	12°	14°	15°	16°	17°	18°	19°	20°	21°	22°	23°	24°	25°	26°	27°	28°	30°
745	12	29	47	83	100	118	136	153	171	189	206	224	242	260	277	295	313	348	365
746	6	23	41	77	94	112	130	147	165	183	200	218	236	254	271	289	307	342	359
747	1	17	34	70	88	105	123	140	158	176	193	210	229	247	264	281	299	334	352
748	8	9	27	63	81	98	116	134	151	169	186	204	222	240	257	274	291	327	344
749	15	2	20	56	74	91	109	127	144	162	178	196	214	232	249	267	284	320	337
750	22	9	31	49	66	84	101	119	137	154	171	189	207	225	242	261	277	313	330
751	27	10	7	43	60	77	95	113	131	148	165	183	201	219	236	255	272	307	323
752	34	17	0	36	45	71	89	106	124	141	158	176	194	212	229	248	264	299	316
753	40	24	6	32	40	58	75	93	110	128	144	162	180	198	215	234	249	284	302
754	48	31	14	23	40	52	69	87	104	122	138	156	174	192	208	228	243	278	295
755	54	36	20	17	34	44	62	79	97	114	131	148	166	184	201	220	236	271	288
756	60	43	26	23	37	44	62	79	97	114	131	148	166	184	201	220	236	271	288
757	68	50	33	29	44	52	69	87	104	122	138	156	174	192	208	228	243	278	288
758	74	57	39	35	44	52	69	87	104	122	138	156	174	192	208	228	243	278	288
759	80	62	45	40	44	52	69	87	104	122	138	156	174	192	208	228	243	278	288
760	86	70	52	47	50	52	69	87	104	122	138	156	174	192	208	228	243	278	288
761	93	77	59	54	56	58	75	93	110	128	144	162	180	198	215	234	249	284	281
762	100	83	66	61	63	65	82	99	117	135	152	169	187	205	222	241	257	291	287
763	105	89	72	67	69	71	88	106	124	141	158	176	194	212	229	248	264	299	295
764	112	95	79	74	76	78	95	113	131	148	165	183	201	219	236	255	272	307	303
765	119	102	85	80	82	84	101	119	137	154	171	189	207	225	242	261	277	313	309
766	125	107	91	86	88	90	107	125	143	161	178	196	214	232	249	267	284	320	316
767	132	115	97	92	94	96	113	131	148	165	183	201	219	236	255	272	289	325	321
768	138	121	104	99	101	103	120	138	156	174	192	210	228	246	264	282	299	335	331
769	144	127	110	105	107	109	126	144	162	180	198	216	234	252	270	288	306	342	338
770	150	133	116	111	113	115	132	150	168	186	204	222	240	258	276	294	312	348	344
771	157	140	124	119	121	123	140	158	176	194	212	230	248	266	284	302	320	356	352
772	163	146	129	124	126	128	145	163	181	199	217	235	253	271	289	307	325	361	357
773	169	152	136	131	133	135	152	170	188	206	224	242	260	278	296	314	332	368	364
774	175	158	141	136	138	140	157	175	193	211	229	247	265	283	301	319	337	373	369
775	182	165	148	143	145	147	164	182	200	218	236	254	272	290	308	326	344	380	376

TABLE XVIII. (*Text*, p. 269.)

Specific Gravities of Solutions of Sulphur in Carbon Bisulphide, with the corresponding weights of Sulphur dissolved by 100 parts by weight of pure Carbon Bisulphide at 15° C., compared with Water at 4° C.

Specific gravity.	Sulphur dissolved.	Specific gravity.	Sulphur dissolved.	Specific gravity.	Sulphur dissolved.	Specific gravity.	Sulphur dissolved.
1.2708	0.0	1.2999	6.4	1.3263	12.8	1.3507	19.2
1.2717	0.2	1.3007	6.6	1.3271	13.0	1.3511	19.4
1.2726	0.4	1.3016	6.8	1.3279	13.2	1.3521	19.6
1.2736	0.6	1.3024	7.0	1.3287	13.4	1.3529	19.8
1.2745	0.8	1.3032	7.2	1.3295	13.6	1.3536	20.0
1.2754	1.0	1.3041	7.4	1.3303	13.8	1.3543	20.2
1.2763	1.2	1.3050	7.6	1.3311	14.0	1.3550	20.4
1.2772	1.4	1.3058	7.8	1.3319	14.2	1.3557	20.6
1.2782	1.6	1.3066	8.0	1.3326	14.4	1.3564	20.8
1.2791	1.8	1.3074	8.2	1.3334	14.6	1.3571	21.0
1.2800	2.0	1.3083	8.4	1.3342	14.8	1.3577	21.2
1.2809	2.2	1.3091	8.6	1.3350	15.0	1.3584	21.4
1.2819	2.4	1.3100	8.8	1.3357	15.2	1.3591	21.6
1.2828	2.6	1.3108	9.0	1.3365	15.4	1.3598	21.8
1.2838	2.8	1.3116	9.2	1.3373	15.6	1.3605	22.0
1.2847	3.0	1.3125	9.4	1.3380	15.8	1.3612	22.2
1.2856	3.2	1.3133	9.6	1.3388	16.0	1.3619	22.4
1.2866	3.4	1.3142	9.8	1.3396	16.2	1.3626	22.6
1.2875	3.6	1.3150	10.0	1.3403	16.4	1.3633	22.8
1.2885	3.8	1.3158	10.2	1.3411	16.6	1.3640	23.0
1.2894	4.0	1.3166	10.4	1.3418	16.8	1.3646	23.2
1.2903	4.2	1.3174	10.6	1.3426	17.0	1.3653	23.4
1.2912	4.4	1.3182	10.8	1.3433	17.2	1.3660	23.6
1.2920	4.6	1.3190	11.0	1.3441	17.4	1.3667	23.8
1.2929	4.8	1.3199	11.2	1.3448	17.6	1.3674	24.0
1.2938	5.0	1.3207	11.4	1.3456	17.8	1.3681	24.2
1.2947	5.2	1.3215	11.6	1.3463	18.0	1.3688	24.4
1.2956	5.4	1.3223	11.8	1.3470	18.2	1.3695	24.6
1.2964	5.6	1.3231	12.0	1.3478	18.4	1.3702	24.8
1.2973	5.8	1.3239	12.2	1.3485	18.6	1.3709	25.0
1.2982	6.0	1.3247	12.4	1.3492	18.8	...	...
1.2990	6.2	1.3255	12.6	1.3500	19.0	...	...

TABLE XIX. (*Text*, p. 305.)

Table of the Specific Gravity of Solutions of Sulphur  
Dioxide in Water.

Specific gravity.	Temp. °C.	Per cent. SO <sub>2</sub> .	Specific gravity.	Temp. °C.	Per cent. SO <sub>2</sub> .
1.0051	15.5	0.99	1.0399	15.5	8.08
1.0102	15.5	2.05	1.0438	15.5	8.68
1.0148	15.5	2.87	1.0492	15.5	9.80
1.0204	15.5	4.04	1.0541	15.5	10.75
1.0252	15.5	4.99	1.0597	12.5	11.65
1.0297	15.5	5.89	1.0668	11	13.09
1.0353	15.5	7.01	...	...	...

TABLE XX. (*Text*, p. 324.)

Table for correcting the Specific Gravity of Nitric Acid for the  
contained Nitric Peroxide.

*Specific Gravity of Initial Acid 1.4960 at 15°/4° (in vacuo).*

N <sub>2</sub> O <sub>4</sub> per cent.	Alteration of the Specific Gravity by N <sub>2</sub> O <sub>4</sub> .	N <sub>2</sub> O <sub>4</sub> per cent.	Alteration of the Specific Gravity by N <sub>2</sub> O <sub>4</sub> .	N <sub>2</sub> O <sub>4</sub> per cent.	Alteration of the Specific Gravity by N <sub>2</sub> O <sub>4</sub> .
0.25	0.00050	4.50	0.02875	8.75	0.05825
0.50	0.00075	4.75	0.03050	9.00	0.06000
0.75	0.00150	5.00	0.03225	9.25	0.06160
1.00	0.00300	5.25	0.03365	9.50	0.06325
1.25	0.00475	5.50	0.03600	9.75	0.06500
1.50	0.00675	5.75	0.03775	10.00	0.06600
1.75	0.00775	6.00	0.03950	10.25	0.06815
2.00	0.01450	6.25	0.04175	10.50	0.06975
2.25	0.01250	6.50	0.04300	10.75	0.07135
2.50	0.01425	6.75	0.04475	11.00	0.07300
2.75	0.01625	7.00	0.04650	11.25	0.07450
3.00	0.01800	7.25	0.04720	11.50	0.07600
3.25	0.01985	7.50	0.05000	11.75	0.07750
3.50	0.02165	7.75	0.05165	12.00	0.07850
3.75	0.02350	8.00	0.05325	12.25	0.08050
4.00	0.02525	8.25	0.05500	12.50	0.08200
4.25	0.02690	8.50	0.05660	12.75	0.08350

## APPENDIX

TABLE XXI. (*Test*, p. 325.)

Table of the Specific Gravity of Nitric Acid of various strengths,  
at 15° C. referred to Water at 4° C.

Spec. Grav. at 15° C. ( <i>in vacuo</i> )	Degrees Baume.	Degrees Twaddell.	100 Parts by weight contain					1 Litre contains gr.				
			$\text{Na}_2\text{O}_2$	$\text{HNO}_3$	Acid of 36° B.	Acid of 40° B.	Acid of 48½° B.	$\text{Na}_2\text{O}_2$	$\text{HNO}_3$	Acid of 36° B.	Acid of 40° B.	Acid of 48½° B.
1.000	0	0	0.08	0.10	0.19	0.16	0.10	0.001	0.001	0.002	0.002	0.001
1.005	0.7	1	0.85	1.00	1.89	1.61	1.03	0.008	0.010	0.019	0.016	0.010
1.010	1.4	2	1.62	1.90	3.60	3.07	1.95	0.016	0.019	0.036	0.031	0.019
1.015	2.1	3	2.39	2.80	5.30	4.52	2.87	0.024	0.028	0.053	0.045	0.029
1.020	2.7	4	3.17	3.70	7.01	5.98	3.79	0.033	0.038	0.072	0.061	0.039
1.025	3.4	5	3.94	4.60	8.71	7.43	4.72	0.040	0.047	0.089	0.076	0.048
1.030	4.1	6	4.71	5.50	10.42	8.88	5.64	0.049	0.057	0.108	0.092	0.058
1.035	4.7	7	5.47	6.38	12.08	10.30	6.54	0.057	0.066	0.125	0.107	0.068
1.040	5.4	8	6.22	7.26	13.75	11.72	7.45	0.064	0.075	0.142	0.121	0.077
1.045	6.0	9	6.97	8.13	15.40	13.13	8.31	0.073	0.085	0.161	0.137	0.087
1.050	6.7	10	7.71	8.99	17.03	14.52	9.22	0.081	0.094	0.178	0.152	0.096
1.055	7.4	11	8.13	9.84	18.64	15.89	10.09	0.089	0.104	0.197	0.168	0.107
1.060	8.0	12	9.15	10.68	20.23	17.25	10.95	0.097	0.113	0.214	0.182	0.116
1.065	8.7	13	9.87	11.51	21.80	18.59	11.81	0.105	0.123	0.233	0.198	0.126
1.070	9.4	14	10.57	12.33	23.35	19.91	12.65	0.113	0.132	0.250	0.213	0.135
1.075	10.0	15	11.27	13.15	24.91	21.24	13.49	0.121	0.141	0.267	0.228	0.145
1.080	10.6	16	11.96	13.95	26.42	22.53	14.31	0.129	0.151	0.286	0.244	0.155
1.085	11.2	17	12.64	14.74	27.92	23.80	15.12	0.137	0.160	0.303	0.258	0.164
1.090	11.9	18	13.31	15.53	29.41	25.03	15.93	0.145	0.169	0.320	0.273	0.173
1.095	12.4	19	13.99	16.32	30.91	26.35	16.74	0.153	0.179	0.339	0.289	0.184
1.100	13.0	20	14.67	17.11	32.41	27.63	17.55	0.161	0.188	0.356	0.304	0.193
1.105	13.6	21	15.34	17.89	33.89	28.89	18.35	0.170	0.198	0.375	0.320	0.203
1.110	14.2	22	16.00	18.67	35.36	30.15	19.15	0.177	0.207	0.392	0.335	0.212
1.115	14.9	23	16.67	19.45	36.84	31.41	19.95	0.186	0.217	0.411	0.350	0.223
1.120	15.4	24	17.34	20.23	38.31	32.67	20.75	0.195	0.227	0.430	0.366	0.233
1.125	16.0	25	18.00	21.00	39.77	33.91	21.54	0.202	0.236	0.447	0.381	0.242
1.130	16.5	26	18.66	21.77	41.23	35.16	22.33	0.211	0.246	0.466	0.397	0.252
1.135	17.1	27	19.32	22.54	42.69	36.40	23.12	0.219	0.256	0.485	0.413	0.263
1.140	17.7	28	19.98	23.31	44.15	37.65	23.91	0.228	0.266	0.504	0.430	0.273
1.145	18.3	29	20.64	24.08	45.61	38.89	24.70	0.237	0.276	0.523	0.446	0.283
1.150	18.8	30	21.29	24.84	47.05	40.12	25.48	0.245	0.286	0.542	0.462	0.293
1.155	19.3	31	21.94	25.60	48.49	41.35	26.26	0.254	0.296	0.561	0.478	0.304
1.160	19.8	32	22.60	26.36	49.92	42.57	27.04	0.262	0.306	0.580	0.494	0.314
1.165	20.3	33	23.25	27.12	51.36	43.80	27.82	0.271	0.316	0.598	0.510	0.324
1.170	20.9	34	23.90	27.88	52.80	45.03	28.59	0.279	0.326	0.617	0.526	0.334
1.175	21.4	35	24.54	28.63	54.22	46.24	29.36	0.288	0.336	0.636	0.543	0.345
1.180	22.0	36	25.18	29.38	55.64	47.45	30.13	0.297	0.347	0.657	0.560	0.356
1.185	22.5	37	25.83	30.13	57.07	48.66	30.90	0.306	0.357	0.676	0.577	0.366
1.190	23.0	38	26.47	30.88	58.49	49.87	31.67	0.315	0.367	0.695	0.593	0.376
1.195	23.5	39	27.10	31.62	59.89	51.07	32.43	0.324	0.378	0.715	0.610	0.388
1.200	24.0	40	27.74	32.36	61.29	52.26	33.19	0.333	0.388	0.735	0.627	0.398
1.205	24.5	41	28.36	33.09	62.67	53.23	33.94	0.342	0.399	0.755	0.644	0.409
1.210	25.0	42	28.99	33.82	64.05	54.21	34.69	0.351	0.409	0.775	0.661	0.419
1.215	25.5	43	29.61	34.55	65.44	55.18	35.44	0.360	0.420	0.795	0.678	0.431
1.220	26.0	44	30.24	35.28	66.82	56.16	36.18	0.369	0.430	0.815	0.695	0.441
1.225	26.4	45	30.88	36.03	68.24	57.64	36.95	0.378	0.441	0.835	0.712	0.452
1.230	26.9	46	31.53	36.78	69.66	59.13	37.72	0.387	0.452	0.856	0.730	0.466
1.235	27.4	47	32.17	37.53	71.08	60.61	38.49	0.397	0.463	0.877	0.748	0.477
1.240	27.9	48	32.82	38.29	72.52	61.84	39.27	0.407	0.475	0.900	0.767	0.487
1.245	28.4	49	33.47	39.05	73.96	63.07	40.05	0.417	0.486	0.921	0.785	0.499
1.250	28.8	50	34.13	39.82	75.42	64.31	40.84	0.427	0.498	0.943	0.804	0.51

Table of the Specific Gravity of Nitric Acid, etc.—Continued.

Spec. Grav. at 15° 4'— (in vacuo).	Degrees Baume.	Degrees Twaddell.	100 Parts by weight contain					1 Litre contains kg.				
			N <sub>2</sub> O <sub>5</sub> .	HNO <sub>3</sub> .	Acid of 86° B.	Acid of 40° B.	Acid of 48½° B.	N <sub>2</sub> O <sub>5</sub> .	HNO <sub>3</sub> .	Acid of 86° B.	Acid of 40° B.	Acid of 48½° B.
1.255	29.3	51	34.78	40.58	76.86	65.54	41.62	0.437	0.509	0.965	0.822	0.522
1.260	29.7	52	35.44	41.34	78.30	66.76	42.40	0.447	0.521	0.987	0.841	0.534
1.265	30.2	53	36.09	42.10	79.74	67.99	43.18	0.457	0.533	1.009	0.860	0.547
1.270	30.6	54	36.75	42.87	81.20	69.23	43.97	0.467	0.544	1.031	0.879	0.558
1.275	31.1	55	37.41	43.64	82.65	70.48	44.76	0.477	0.556	1.054	0.898	0.570
1.280	31.5	56	38.07	44.41	84.11	71.72	45.55	0.487	0.568	1.077	0.918	0.583
1.285	32.0	57	38.73	45.18	85.57	72.96	46.34	0.498	0.581	1.100	0.938	0.596
1.290	32.4	58	39.39	45.95	87.03	74.21	47.13	0.508	0.593	1.123	0.957	0.608
1.295	32.8	59	40.05	46.72	88.48	75.45	47.92	0.519	0.605	1.146	0.977	0.621
1.300	33.3	60	40.71	47.49	89.94	76.70	48.71	0.529	0.617	1.169	0.997	0.633
1.305	33.7	61	41.37	48.26	91.40	77.94	49.50	0.540	0.630	1.193	1.017	0.646
1.310	34.2	62	42.06	49.07	92.94	79.25	50.33	0.551	0.643	1.218	1.038	0.659
1.315	34.6	63	42.76	49.89	94.49	80.57	51.17	0.562	0.656	1.243	1.059	0.673
1.320	35.0	64	43.47	50.71	96.05	81.90	52.01	0.573	0.669	1.268	1.080	0.686
1.325	35.4	65	44.17	51.53	97.60	83.22	52.85	0.585	0.683	1.294	1.103	0.701
1.330	35.8	66	44.89	52.37	99.19	84.58	53.71	0.597	0.697	1.320	1.126	0.715
1.3325	36.0	66.5	45.26	52.80	100.00	85.27	54.15	0.603	0.704	1.333	1.137	0.722
1.335	36.2	67	45.62	53.22	100.80	85.95	54.58	0.609	0.710	1.346	1.148	0.728
1.340	36.6	68	46.35	54.07	102.41	87.32	55.46	0.621	0.725	1.373	1.171	0.744
1.345	37.0	69	47.08	54.93	104.04	88.71	56.34	0.633	0.739	1.400	1.193	0.758
1.350	37.4	70	47.82	55.79	105.67	90.10	57.22	0.645	0.753	1.427	1.216	0.772
1.355	37.8	71	48.57	56.66	107.31	91.51	58.11	0.658	0.768	1.455	1.240	0.788
1.360	38.2	72	49.35	57.57	109.03	92.97	59.05	0.671	0.783	1.483	1.265	0.803
1.365	38.6	73	50.13	58.48	110.75	94.44	59.98	0.684	0.798	1.513	1.289	0.818
1.370	39.0	74	50.91	59.39	112.48	95.91	60.91	0.698	0.814	1.543	1.314	0.835
1.375	39.4	75	51.69	60.30	114.20	97.38	61.85	0.711	0.829	1.573	1.339	0.850
1.380	39.8	76	52.52	61.27	116.04	98.95	62.84	0.725	0.846	1.603	1.366	0.868
1.3833	40.0	...	53.08	61.92	117.27	100.00	63.51	0.735	0.857	1.623	1.383	0.879
1.385	40.1	77	53.35	62.24	117.88	100.51	63.84	0.739	0.862	1.633	1.392	0.884
1.390	40.5	78	54.20	63.23	119.75	102.12	64.85	0.753	0.879	1.665	1.420	0.902
1.395	40.8	79	55.07	64.25	121.68	103.76	65.90	0.768	0.896	1.697	1.447	0.919
1.400	41.2	80	55.97	65.30	123.67	105.46	66.97	0.783	0.914	1.731	1.476	0.937
1.405	41.6	81	56.92	66.40	125.75	107.24	68.10	0.800	0.933	1.767	1.507	0.957
1.410	42.0	82	57.86	67.50	127.84	109.01	69.23	0.816	0.952	1.803	1.537	0.976
1.415	42.3	83	58.83	68.63	129.98	110.84	70.39	0.832	0.971	1.839	1.568	0.996
1.420	42.7	84	59.83	69.80	132.19	112.73	71.59	0.849	0.991	1.877	1.600	1.016
1.425	43.1	85	60.84	70.98	134.43	114.63	72.80	0.867	1.011	1.915	1.633	1.037
1.430	43.4	86	61.86	72.17	136.68	116.55	74.02	0.885	1.032	1.955	1.667	1.058
1.435	43.8	87	62.91	73.39	138.99	118.52	75.27	0.903	1.053	1.995	1.701	1.080
1.440	44.1	88	64.01	74.68	141.44	120.61	76.59	0.921	1.075	2.037	1.736	1.103
1.445	44.4	89	65.13	75.98	143.90	122.71	77.93	0.941	1.098	2.080	1.773	1.126
1.450	44.8	90	66.24	77.28	146.38	124.81	79.26	0.961	1.121	2.123	1.810	1.150
1.455	45.1	91	67.38	78.60	148.86	126.94	80.62	0.981	1.144	2.167	1.848	1.173
1.460	45.4	92	68.56	79.98	151.47	129.17	82.03	1.001	1.168	2.212	1.886	1.198
1.465	45.8	93	69.79	81.42	154.20	131.49	83.51	1.023	1.193	2.259	1.927	1.224
1.470	46.1	94	71.06	82.90	157.00	133.88	85.03	1.045	1.219	2.309	1.969	1.250
1.475	46.4	95	72.39	84.45	159.94	136.39	86.62	1.068	1.246	2.360	2.012	1.278
1.480	46.8	96	73.76	86.05	162.97	138.97	88.26	1.092	1.274	2.413	2.058	1.307
1.485	47.1	97	75.18	87.70	166.09	141.63	89.95	1.116	1.302	2.466	2.103	1.335
1.490	47.4	98	76.60	89.60	169.69	144.70	91.90	1.144	1.335	2.528	2.156	1.369
1.495	47.8	99	78.52	91.60	173.48	147.93	93.95	1.174	1.369	2.593	2.211	1.404
1.500	48.1	100	80.65	94.09	178.19	151.96	96.50	1.210	1.411	2.672	2.278	1.447



Table of the Specific Gravity of Nitric Acid, etc.—(Continued).

Spec. Grav. at 15° 4° ( <i>in vacuo</i> ).	Degrees Baumé.	Degrees Twaddell.	100 Parts by weight contain					1 Litre contains gts.				
			$\text{N}_2\text{O}_5$	$\text{HNO}_3$	Acid of 36° B.	Acid of 40° B.	Acid of 48° B.	$\text{N}_2\text{O}_5$	$\text{HNO}_3$	Acid of 36° B.	Acid of 40° B.	Acid of 48° B.
1.501	...	...	81.09	94.60	179.16	152.78	97.03	1.217	1.420	2.689	2.293	1.456
1.502	...	...	81.50	95.08	180.07	153.55	97.52	1.224	1.428	2.704	2.306	1.465
1.503	...	...	81.91	95.55	180.96	154.31	98.00	1.231	1.435	2.720	2.319	1.473
1.504	...	...	82.29	96.00	181.81	155.04	98.46	1.238	1.444	2.735	2.332	1.481
1.505	48.4	101	82.63	96.39	182.55	155.67	98.86	1.244	1.451	2.748	2.343	1.488
1.506	...	...	82.94	96.76	183.25	156.27	99.27	1.249	1.457	2.759	2.353	1.494
1.507	...	...	83.26	97.13	183.95	156.86	99.62	1.255	1.464	2.773	2.364	1.502
1.508	48.5	...	83.58	97.50	184.35	157.47	100.00	1.260	1.470	2.784	2.374	1.508
1.509	...	...	83.87	97.84	185.30	158.01	100.35	1.265	1.476	2.795	2.384	1.514
1.510	48.7	102	84.09	98.10	185.79	158.43	100.62	1.270	1.481	2.805	2.392	1.519
1.511	...	...	84.28	98.32	186.21	158.79	100.84	1.274	1.486	2.814	2.400	1.524
1.512	...	...	84.46	98.53	186.61	159.13	101.06	1.277	1.490	2.822	2.406	1.528
1.513	...	...	84.63	98.73	186.98	159.45	101.26	1.280	1.494	2.829	2.413	1.532
1.514	...	...	84.78	98.90	187.30	159.72	101.44	1.283	1.497	2.835	2.418	1.535
1.515	49.0	103	84.92	99.07	187.63	160.00	101.61	1.287	1.501	2.843	2.424	1.539
1.516	...	...	85.04	99.21	187.89	160.22	101.75	1.289	1.504	2.848	2.429	1.543
1.517	...	...	85.15	99.34	188.14	160.43	101.89	1.292	1.507	2.854	2.434	1.546
1.518	...	...	85.26	99.46	188.37	160.63	102.01	1.294	1.510	2.860	2.439	1.549
1.519	...	...	85.35	99.57	188.58	160.81	102.12	1.296	1.512	2.864	2.442	1.551
1.520	49.4	104	85.44	99.67	188.77	160.97	102.23	1.299	1.515	2.869	2.447	1.554

TABLE XXII. (*Text*, p. 327.)

Table for the Correction of the observed Specific Gravity of Nitric Acid for differences of Temperature between 13° and 17° C.

Specific Gravity.	Correction for $\pm 1^\circ$ .	Specific Gravity.	Correction for $\pm 1^\circ$ .
1.000—1.020	$\pm 0.0001$	1.281—1.310	$\pm 0.0010$
1.021—1.040	0.0002	1.311—1.350	0.0011
1.041—1.070	0.0003	1.351—1.385	0.0012
1.071—1.100	0.0004	1.386—1.400	0.0013
1.101—1.130	0.0005	1.401—1.435	0.0014
1.131—1.161	0.0006	1.436—1.490	0.0015
1.162—1.200	0.0007	1.491—1.500	0.0016
1.201—1.245	0.0008	1.501—1.520	0.0017
1.246—1.280	0.0009		

TABLE XXIII. (*Text*, p. 344.)

Table for the estimation of Nitrous Acid in Nitrous Vitriol.

Expressed as  $\text{HNO}_3$ ,  $\text{NaNO}_3$ , and as nitric acid of  $66^\circ\cdot 5$  and  $77^\circ$  Tw. at  $15^\circ\text{C}$ ., in which 50 c.c.  $\text{KMnO}_4$  potassium permanganate is taken for the titration, and the percentages by weight are based on sulphuric acid of  $140^\circ$  Tw. as unit.

Acid required. % c.c.	$\text{HNO}_3$ .		$\text{NaNO}_3$ .		Nitric Acid $66^\circ\cdot 5$ Tw.		Nitric Acid $77^\circ$ Tw.	
	a. G. per Litre.	b. Percentage by Weight.	a. G. per Litre.	b. Percentage by Weight.	a. G. per Litre.	b. Percentage by Weight.	a. G. per Litre.	b. Percentage by Weight.
10	78.8	4.61	106.3	6.22	149.1	8.72	127.2	7.44
11	71.6	4.19	96.6	5.65	135.6	7.93	115.6	6.76
12	65.6	3.84	88.6	5.18	124.3	7.27	106.0	6.20
13	60.6	3.54	81.8	4.78	114.7	6.70	97.8	5.72
14	56.2	3.29	75.9	4.44	106.5	6.23	90.8	5.31
15	52.5	3.07	70.9	4.14	99.4	5.80	84.8	4.96
16	49.2	2.88	66.4	3.88	93.2	5.45	79.5	4.65
17	46.3	2.71	62.5	3.65	87.7	5.13	74.8	4.37
18	43.7	2.56	59.0	3.45	82.9	4.85	70.7	4.13
19	41.5	2.42	55.9	3.27	78.5	4.59	66.9	3.91
20	39.4	2.30	53.1	3.11	74.6	4.36	63.6	3.72
21	37.5	2.19	50.6	2.96	71.0	4.15	60.6	3.54
22	35.8	2.09	48.3	2.82	67.8	3.96	57.8	3.38
23	34.2	2.00	46.2	2.70	64.8	3.79	55.3	3.23
24	32.8	1.92	44.3	2.60	62.1	3.62	53.0	3.11
25	31.5	1.84	42.5	2.49	59.7	3.49	50.8	2.97
26	30.3	1.77	40.9	2.39	57.4	3.35	48.9	2.86
27	29.2	1.71	39.4	2.30	55.2	3.25	47.1	2.75
28	28.1	1.65	38.0	2.22	53.3	3.12	45.4	2.66
29	27.1	1.59	36.7	2.15	51.4	3.01	43.9	2.56
30	26.3	1.54	35.4	2.07	49.7	2.91	42.4	2.48
31	25.4	1.49	34.3	2.01	48.1	2.81	41.0	2.40
32	24.6	1.44	33.2	1.94	46.6	2.73	39.7	2.32
33	23.9	1.40	32.2	1.88	45.2	2.64	38.5	2.25
34	23.2	1.35	31.3	1.84	43.9	2.56	37.4	2.19
35	22.5	1.32	30.4	1.78	42.6	2.49	36.3	2.13
36	21.9	1.28	29.5	1.73	41.4	2.42	35.3	2.07
37	21.3	1.24	28.7	1.68	40.3	2.36	34.4	2.01
38	20.7	1.21	28.0	1.64	39.3	2.30	33.5	1.96
39	20.2	1.18	27.3	1.60	38.2	2.23	32.6	1.91
40	19.7	1.15	26.5	1.55	37.3	2.18	31.8	1.86
41	19.2	1.12	25.8	1.51	36.4	2.13	31.0	1.81
42	18.8	1.10	25.3	1.48	35.5	2.08	30.3	1.77
43	18.3	1.07	24.7	1.45	34.6	2.02	29.5	1.73
44	17.9	1.05	24.2	1.42	33.9	1.98	28.9	1.69
45	17.5	1.02	23.6	1.38	33.1	1.93	28.2	1.65
46	17.1	1.00	23.1	1.35	32.4	1.90	27.6	1.62
47	16.7	0.98	22.6	1.32	31.7	1.85	27.0	1.58
48	16.4	0.96	22.2	1.30	31.1	1.82	26.5	1.55
49	16.1	0.94	21.7	1.27	30.4	1.78	25.9	1.51
50	15.8	0.921	21.3	1.25	29.8	1.74	25.4	1.49
55	14.3	0.837	19.3	1.13	27.1	1.59	23.1	1.35
60	13.1	0.768	17.7	1.04	24.5	1.45	21.2	1.24
65	12.1	0.709	16.4	0.96	22.9	1.34	19.6	1.14
70	11.2	0.653	15.2	0.89	21.3	1.25	18.2	1.06
75	10.5	0.614	14.17	0.829	19.9	1.16	16.96	0.99
80	9.85	0.576	13.3	0.778	18.6	1.09	15.9	0.93
85	9.2	0.542	12.5	0.731	17.5	1.03	14.9	0.87
90	8.7	0.511	11.8	0.692	16.5	0.967	14.1	0.825
95	8.3	0.485	11.2	0.655	15.7	0.913	13.4	0.783
100	7.9	0.461	10.6	0.620	14.9	0.875	12.7	0.744

TABLE XXIV. (*Text*, p. 315.)

Table for calculating Volumes of Nitric Oxide to Weights of Nitrogen, Nitric Oxide, Nitrous Acid, Nitric Acid, and Sodium Nitrate.

c.c. NO.	N.		NO.		N <sub>2</sub> O <sub>5</sub>	
	a. mg.	b. Percentage.	a. mg.	b. Percentage.	a. mg.	b. Percentage.
1	0.6257	0.0366	1.3402	0.0784	1.6975	0.0993
2	1.2514	0.0732	2.6804	0.1568	3.3950	0.1986
3	1.8771	0.1098	4.0206	0.2352	5.0925	0.2979
4	2.5028	0.1464	5.3608	0.3136	6.7900	0.3972
5	3.1285	0.1830	6.7010	0.3920	8.4875	0.4965
6	3.7542	0.2196	8.0412	0.4704	10.1850	0.5958
7	4.3799	0.2562	9.3814	0.5488	11.8825	0.6951
8	5.0056	0.2928	10.7216	0.6272	13.5800	0.7944
9	5.6313	0.3294	12.0618	0.7056	15.2775	0.8937

c.c. NO.	HNO <sub>3</sub>		Nitric Acid 60% Tw.		NaNO <sub>3</sub>	
	a. mg.	b. Percentage.	a. mg.	b. Percentage.	a. mg.	b. Percentage.
1	2.8144	0.1646	5.333	0.312	3.7986	0.2221
2	5.6288	0.3292	10.666	0.624	7.5972	0.4442
3	8.4432	0.4938	15.999	0.936	11.3958	0.6663
4	11.2576	0.6584	21.332	1.248	15.1944	0.8884
5	14.0720	0.8230	26.665	1.560	18.9930	1.1105
6	16.8864	0.9876	31.998	1.872	22.7916	1.3326
7	19.7008	1.1522	37.331	2.184	26.5902	1.5547
8	22.5152	1.3168	42.664	2.496	30.3888	1.7768
9	25.3296	1.4814	47.997	2.808	34.1874	1.9989

TABLE XXV. (*Text*, p. 348.)

Table for determining the Specific Gravity of Pure Sulphuric  
 • Acid-water Mixtures from the Percentage Content.

Per cent. Sulphuric Acid.	0	1	2	3	4	5	6	7	8	9
	Density of Sulphuric Acid at +15° C. compared with Water at +4° C. for percentages given in units in the vertical column at the side, and in decimal parts in the horizontal line above.									
0	0.9991	0.9998	1.0005	1.0012	1.0019	1.0026	1.0033	1.0040	1.0047	1.0054
1	1.0061	1.0068	1.0079	1.0082	1.0088	1.0095	1.0102	1.0109	1.0116	1.0122
2	1.0129	1.0136	1.0143	1.0149	1.0156	1.0163	1.0170	1.0176	1.0183	1.0190
3	1.0197	1.0203	1.0210	1.0217	1.0224	1.0230	1.0237	1.0244	1.0251	1.0257
4	1.0264	1.0271	1.0277	1.0284	1.0291	1.0298	1.0304	1.0311	1.0318	1.0325
5	1.0332	1.0338	1.0345	1.0352	1.0359	1.0366	1.0373	1.0380	1.0386	1.0393
6	1.0400	1.0407	1.0414	1.0421	1.0428	1.0435	1.0442	1.0449	1.0456	1.0462
7	1.0469	1.0476	1.0483	1.0490	1.0497	1.0504	1.0511	1.0518	1.0525	1.0532
8	1.0539	1.0546	1.0554	1.0561	1.0568	1.0575	1.0582	1.0589	1.0596	1.0603
9	1.0610	1.0617	1.0624	1.0631	1.0638	1.0645	1.0653	1.0660	1.0667	1.0674
10	1.0681	1.0688	1.0695	1.0702	1.0710	1.0717	1.0724	1.0731	1.0738	1.0745
11	1.0753	1.0760	1.0767	1.0774	1.0781	1.0789	1.0796	1.0803	1.0810	1.0818
12	1.0825	1.0832	1.0839	1.0847	1.0854	1.0861	1.0868	1.0876	1.0883	1.0890
13	1.0898	1.0905	1.0912	1.0920	1.0927	1.0934	1.0942	1.0949	1.0956	1.0964
14	1.0971	1.0978	1.0986	1.0993	1.1000	1.1008	1.1015	1.1023	1.1030	1.1038
15	1.1045	1.1052	1.1060	1.1067	1.1075	1.1082	1.1090	1.1097	1.1105	1.1112
16	1.1120	1.1127	1.1135	1.1142	1.1150	1.1157	1.1165	1.1172	1.1180	1.1187
17	1.1195	1.1202	1.1210	1.1217	1.1225	1.1233	1.1240	1.1248	1.1255	1.1263
18	1.1270	1.1278	1.1286	1.1293	1.1301	1.1309	1.1316	1.1324	1.1331	1.1339
19	1.1347	1.1354	1.1362	1.1370	1.1377	1.1385	1.1393	1.1400	1.1408	1.1416
20	1.1424	1.1431	1.1439	1.1447	1.1454	1.1462	1.1470	1.1478	1.1485	1.1493
21	1.1501	1.1509	1.1516	1.1524	1.1532	1.1540	1.1548	1.1555	1.1563	1.1571
22	1.1579	1.1587	1.1594	1.1602	1.1610	1.1618	1.1626	1.1634	1.1641	1.1649
23	1.1657	1.1665	1.1673	1.1681	1.1689	1.1697	1.1705	1.1712	1.1720	1.1728
24	1.1736	1.1744	1.1752	1.1760	1.1768	1.1776	1.1784	1.1792	1.1800	1.1808
25	1.1816	1.1824	1.1832	1.1840	1.1848	1.1856	1.1864	1.1872	1.1880	1.1888
26	1.1896	1.1904	1.1912	1.1920	1.1928	1.1936	1.1944	1.1952	1.1960	1.1968
27	1.1976	1.1984	1.1992	1.2000	1.2008	1.2016	1.2025	1.2033	1.2041	1.2049
28	1.2057	1.2065	1.2073	1.2081	1.2089	1.2098	1.2106	1.2114	1.2122	1.2130
29	1.2138	1.2146	1.2155	1.2163	1.2171	1.2179	1.2187	1.2196	1.2204	1.2212
30	1.2220	1.2228	1.2237	1.2245	1.2253	1.2261	1.2270	1.2278	1.2286	1.2294
31	1.2302	1.2311	1.2319	1.2327	1.2335	1.2344	1.2352	1.2360	1.2368	1.2377
32	1.2385	1.2393	1.2402	1.2410	1.2418	1.2426	1.2435	1.2443	1.2451	1.2460
33	1.2468	1.2476	1.2485	1.2493	1.2501	1.2510	1.2518	1.2526	1.2535	1.2543
34	1.2552	1.2560	1.2568	1.2577	1.2585	1.2594	1.2602	1.2610	1.2619	1.2627
35	1.2636	1.2644	1.2653	1.2661	1.2670	1.2678	1.2686	1.2695	1.2703	1.2712
36	1.2720	1.2729	1.2737	1.2746	1.2754	1.2763	1.2771	1.2780	1.2788	1.2797
37	1.2806	1.2814	1.2823	1.2831	1.2840	1.2848	1.2857	1.2866	1.2874	1.2883
38	1.2891	1.2900	1.2908	1.2917	1.2926	1.2935	1.2943	1.2952	1.2961	1.2969
39	1.2978	1.2987	1.2995	1.3004	1.3013	1.3022	1.3030	1.3039	1.3048	1.3057

## Spec. Grav. of Pure Sulphuric Acid-water Mixtures, etc.—Continued.

Per cent. Sulphuric Acid.	0	1	2	3	4	5	6	7	8	9
Density of Sulphuric Acid at +15 C. compared with Water at +4 C. for percentages given in units in the vertical column at the side, and in decimal parts in the horizontal line above.										
40	1.3065	1.3074	1.3083	1.3092	1.3101	1.3109	1.3118	1.3127	1.3136	1.3145
41	1.3153	1.3162	1.3171	1.3180	1.3189	1.3198	1.3207	1.3215	1.3224	1.3233
42	1.3242	1.3251	1.3260	1.3269	1.3278	1.3287	1.3296	1.3305	1.3314	1.3323
43	1.3332	1.3341	1.3350	1.3359	1.3368	1.3377	1.3386	1.3395	1.3404	1.3413
44	1.3423	1.3432	1.3441	1.3450	1.3459	1.3468	1.3478	1.3487	1.3496	1.3505
45	1.3514	1.3524	1.3533	1.3542	1.3551	1.3561	1.3570	1.3579	1.3589	1.3598
46	1.3607	1.3617	1.3626	1.3635	1.3645	1.3654	1.3664	1.3673	1.3682	1.3692
47	1.3701	1.3711	1.3720	1.3730	1.3739	1.3749	1.3758	1.3768	1.3777	1.3787
48	1.3796	1.3806	1.3816	1.3825	1.3835	1.3844	1.3854	1.3864	1.3873	1.3883
49	1.3893	1.3902	1.3912	1.3922	1.3931	1.3941	1.3951	1.3961	1.3970	1.3980
50	1.3990	1.4000	1.4010	1.4019	1.4029	1.4039	1.4049	1.4059	1.4069	1.4079
51	1.4088	1.4098	1.4108	1.4118	1.4128	1.4138	1.4148	1.4158	1.4168	1.4178
52	1.4188	1.4198	1.4208	1.4218	1.4228	1.4238	1.4249	1.4259	1.4269	1.4279
53	1.4289	1.4299	1.4309	1.4319	1.4330	1.4340	1.4350	1.4360	1.4370	1.4381
54	1.4391	1.4401	1.4411	1.4422	1.4432	1.4442	1.4453	1.4463	1.4473	1.4484
55	1.4494	1.4504	1.4515	1.4525	1.4535	1.4546	1.4556	1.4567	1.4577	1.4587
56	1.4598	1.4608	1.4619	1.4629	1.4640	1.4650	1.4661	1.4671	1.4682	1.4692
57	1.4703	1.4714	1.4724	1.4735	1.4745	1.4756	1.4767	1.4777	1.4788	1.4798
58	1.4809	1.4820	1.4837	1.4841	1.4852	1.4863	1.4873	1.4884	1.4895	1.4905
59	1.4916	1.4927	1.4938	1.4949	1.4960	1.4970	1.4981	1.4992	1.5003	1.5013
60	1.5024	1.5035	1.5046	1.5057	1.5068	1.5079	1.5090	1.5101	1.5112	1.5122
61	1.5133	1.5144	1.5155	1.5166	1.5177	1.5188	1.5199	1.5210	1.5221	1.5232
62	1.5243	1.5254	1.5265	1.5276	1.5287	1.5298	1.5309	1.5321	1.5332	1.5343
63	1.5354	1.5365	1.5376	1.5387	1.5398	1.5410	1.5421	1.5432	1.5443	1.5454
64	1.5465	1.5477	1.5488	1.5499	1.5510	1.5521	1.5533	1.5544	1.5555	1.5566
65	1.5578	1.5589	1.5600	1.5612	1.5623	1.5634	1.5645	1.5657	1.5668	1.5679
66	1.5691	1.5702	1.5713	1.5725	1.5736	1.5748	1.5759	1.5770	1.5782	1.5793
67	1.5805	1.5816	1.5827	1.5839	1.5850	1.5862	1.5873	1.5885	1.5896	1.5908
68	1.5919	1.5931	1.5942	1.5954	1.5965	1.5977	1.5989	1.6000	1.6012	1.6023
69	1.6035	1.6046	1.6058	1.6070	1.6081	1.6093	1.6104	1.6116	1.6128	1.6139
70	1.6151	1.6163	1.6174	1.6186	1.6198	1.6209	1.6221	1.6233	1.6245	1.6256
71	1.6268	1.6280	1.6291	1.6303	1.6315	1.6327	1.6338	1.6350	1.6362	1.6374
72	1.6385	1.6397	1.6409	1.6421	1.6433	1.6444	1.6456	1.6468	1.6480	1.6492
73	1.6503	1.6515	1.6527	1.6539	1.6551	1.6563	1.6574	1.6586	1.6598	1.6610
74	1.6622	1.6634	1.6645	1.6657	1.6669	1.6681	1.6693	1.6705	1.6717	1.6728
75	1.6740	1.6752	1.6764	1.6776	1.6788	1.6799	1.6811	1.6823	1.6835	1.6847
76	1.6858	1.6870	1.6882	1.6894	1.6906	1.6917	1.6929	1.6941	1.6953	1.6965
77	1.6976	1.6988	1.7000	1.7012	1.7023	1.7035	1.7047	1.7058	1.7070	1.7082
78	1.7093	1.7105	1.7117	1.7128	1.7140	1.7151	1.7163	1.7175	1.7186	1.7198
79	1.7209	1.7221	1.7232	1.7244	1.7255	1.7267	1.7278	1.7289	1.7301	1.7312
80	1.7324	1.7335	1.7346	1.7357	1.7369	1.7380	1.7391	1.7402	1.7413	1.7424
81	1.7435	1.7446	1.7457	1.7468	1.7479	1.7490	1.7501	1.7512	1.7523	1.7534
82	1.7544	1.7555	1.7566	1.7576	1.7587	1.7597	1.7608	1.7618	1.7628	1.7639
83	1.7649	1.7659	1.7669	1.7679	1.7689	1.7699	1.7709	1.7719	1.7729	1.7738
84	1.7748	1.7758	1.7767	1.7777	1.7786	1.7796	1.7805	1.7814	1.7823	1.7832

Spec. Grav. of Pure Sulphuric Acid-water Mixtures, etc.—*Continued.*

Per cent. Sulphuric Acid.	0	1	2	3	4	5	6	7	8	9
Density of Sulphuric Acid at +15° C. compared with Water at +4° C. for percentages given in units in the vertical column at the side, and in decimal parts in the horizontal line above.										
85	1.7841	1.7850	1.7859	1.7868	1.7876	1.7885	1.7894	1.7902	1.7911	1.7919
86	1.7927	1.7935	1.7943	1.7951	1.7959	1.7967	1.7975	1.7983	1.7991	1.7998
87	1.8006	1.8013	1.8021	1.8028	1.8035	1.8042	1.8049	1.8056	1.8063	1.8070
88	1.8077	1.8084	1.8090	1.8097	1.8103	1.8110	1.8116	1.8122	1.8129	1.8135
89	1.8141	1.8147	1.8153	1.8158	1.8164	1.8170	1.8176	1.8181	1.8187	1.8192
90	1.8198	1.8203	1.8208	1.8213	1.8219	1.8224	1.8229	1.8234	1.8239	1.8244
91	1.8248	1.8253	1.8258	1.8262	1.8267	1.8271	1.8276	1.8280	1.8284	1.8289
92	1.8293	1.8297	1.8301	1.8305	1.8309	1.8313	1.8317	1.8320	1.8324	1.8328
93	1.8331	1.8335	1.8338	1.8341	1.8345	1.8348	1.8351	1.8354	1.8357	1.8360
94	1.8363	1.8366	1.8369	1.8371	1.8374	1.8376	1.8379	1.8381	1.8384	1.8386
95	1.8388	1.8390	1.8392	1.8394	1.8396	1.8398	1.8400	1.8401	1.8403	1.8404
96	1.8406	1.8407	1.8408	1.8409	1.8410	1.8411	1.8412	1.8413	1.8414	1.8414
97	1.8414	1.8415	1.8415	1.8415	1.8415	1.8415	1.8414	1.8414	1.8413	1.8412
98	1.8411	1.8410	1.8409	1.8408	1.8406	1.8405	1.8403	1.8401	1.8398	1.8396
99	1.8393	1.8391	1.8388	1.8385	1.8381	1.8378	(1.8374)	(1.8370)	(1.8366)	(1.8362)
100	(1.8357)	...	...	...	...	...	...	...	...	...

(The bracketed values from 99.6 to 100 per cent. are extrapolated.)

TABLE XXVI. (*Text*, p. 350.)Specific Gravity of Sulphuric Acid Solutions.  
Lunge, Isler, and Naef.

Sp. Gr. at 15° 4° ( <i>in vacuo</i> )	Degrees Baumé.	Degrees Twaddell.	100 parts by weight of chemically pure Acid contain per cent.				1 Litre of chemically pure Acid contains kilograms of			
			SO <sub>3</sub> .	H <sub>2</sub> SO <sub>4</sub> .	Acid of 142° Tw.	Acid of 106° Tw.	SO <sub>3</sub> .	H <sub>2</sub> SO <sub>4</sub> .	Acid of 142° Tw.	Acid of 106° Tw.
1.000	0	0	0.07	0.09	0.12	0.14	0.001	0.001	0.001	0.001
1.005	0.7	1	0.77	0.95	1.21	1.52	0.008	0.009	0.013	0.015
1.010	1.4	2	1.28	1.57	2.01	2.51	0.013	0.016	0.020	0.025
1.015	2.1	3	1.88	2.30	2.95	3.68	0.019	0.023	0.030	0.037
1.020	2.7	4	2.47	3.03	3.88	4.85	0.025	0.031	0.040	0.050
1.025	3.4	5	3.07	3.76	4.82	6.02	0.032	0.039	0.049	0.062
1.030	4.1	6	3.67	4.49	5.78	7.18	0.038	0.046	0.059	0.074
1.035	4.7	7	4.27	5.23	6.73	8.37	0.044	0.054	0.070	0.087
1.040	5.4	8	4.87	5.96	7.64	9.54	0.051	0.062	0.079	0.099
1.045	6.0	9	5.45	6.67	8.55	10.67	0.057	0.071	0.089	0.112
1.050	6.7	10	6.02	7.37	9.44	11.79	0.063	0.077	0.099	0.124
1.055	7.4	11	6.59	8.07	10.34	12.91	0.070	0.085	0.109	0.136
1.060	8.0	12	7.16	8.77	11.24	14.03	0.076	0.093	0.119	0.149
1.065	8.7	13	7.73	9.47	12.14	15.15	0.082	0.102	0.129	0.161
1.070	9.4	14	8.32	10.19	13.05	16.30	0.089	0.109	0.140	0.174
1.075	10.0	15	8.90	10.90	13.96	17.44	0.096	0.117	0.150	0.188

## Specific Gravity of Sulphuric Acid Solutions—Continued.

Sp. Gr. at 15° 4° ( <i>in vacuo</i> ).	Degrees Baumé.	Degrees Twaddell.	100 parts by weight of chemically pure acid contain per cent.				1 Litre of chemically pure acid contains kilograms of			
			SO <sub>3</sub> .	H <sub>2</sub> SO <sub>4</sub> .	Acid of 142° Tw.	Acid of 166° Tw.	SO <sub>3</sub> .	H <sub>2</sub> SO <sub>4</sub> .	Acid of 142° Tw.	Acid of 166° Tw.
1.080	10.6	16	9.47	11.60	14.87	18.56	0.103	0.125	0.161	0.201
1.085	11.2	17	10.04	12.36	15.76	19.69	0.109	0.133	0.171	0.213
1.090	11.9	18	10.60	12.99	16.65	20.78	0.116	0.142	0.181	0.227
1.095	12.4	19	11.16	13.67	17.52	21.87	0.122	0.150	0.192	0.240
1.100	13.0	20	11.71	14.35	18.39	22.96	0.129	0.158	0.202	0.253
1.105	13.6	21	12.27	15.03	19.26	24.05	0.136	0.166	0.212	0.265
1.110	14.2	22	12.82	15.71	20.13	25.14	0.143	0.175	0.223	0.279
1.115	14.9	23	13.36	16.36	20.96	26.18	0.149	0.183	0.234	0.292
1.120	15.4	24	13.89	17.01	21.80	27.22	0.156	0.191	0.245	0.305
1.125	16.0	25	14.42	17.66	22.63	28.26	0.162	0.199	0.255	0.318
1.130	16.5	26	14.95	18.31	23.47	29.30	0.169	0.207	0.265	0.331
1.135	17.1	27	15.48	18.96	24.29	30.34	0.176	0.215	0.276	0.344
1.140	17.7	28	16.01	19.61	25.13	31.38	0.183	0.223	0.287	0.358
1.145	18.3	29	16.54	20.26	25.96	32.42	0.189	0.231	0.297	0.371
1.150	18.8	30	17.07	20.91	26.79	33.46	0.196	0.239	0.308	0.385
1.155	19.3	31	17.59	21.55	27.61	34.48	0.203	0.248	0.319	0.398
1.160	19.8	32	18.11	22.19	28.43	35.50	0.210	0.257	0.330	0.412
1.165	20.3	33	18.64	22.83	29.25	36.53	0.217	0.266	0.341	0.426
1.170	20.9	34	19.16	23.47	30.07	37.55	0.224	0.275	0.352	0.439
1.175	21.4	35	19.69	24.12	30.90	38.59	0.231	0.283	0.363	0.453
1.180	22.0	36	20.21	24.76	31.73	39.62	0.238	0.292	0.374	0.467
1.185	22.5	37	20.73	25.40	32.55	40.64	0.246	0.301	0.386	0.481
1.190	23.0	38	21.26	26.04	33.37	41.66	0.253	0.310	0.397	0.496
1.195	23.5	39	21.78	26.68	34.19	42.69	0.260	0.319	0.409	0.511
1.200	24.0	40	22.30	27.32	35.01	43.71	0.268	0.328	0.420	0.525
1.205	24.5	41	22.82	27.95	35.83	44.72	0.275	0.337	0.432	0.539
1.210	25.0	42	23.33	28.58	36.66	45.73	0.282	0.346	0.444	0.553
1.215	25.5	43	23.84	29.21	37.45	46.74	0.290	0.355	0.455	0.568
1.220	26.0	44	24.36	29.84	38.23	47.74	0.297	0.364	0.466	0.583
1.225	26.4	45	24.88	30.48	39.05	48.77	0.305	0.373	0.478	0.598
1.230	26.9	46	25.39	31.11	39.86	49.78	0.312	0.382	0.490	0.612
1.235	27.4	47	25.88	31.70	40.61	50.72	0.320	0.391	0.502	0.626
1.240	27.9	48	26.35	32.28	41.37	51.65	0.327	0.400	0.513	0.640
1.245	28.4	49	26.83	32.86	42.11	52.58	0.334	0.409	0.524	0.655
1.250	28.8	50	27.29	33.43	42.84	53.49	0.341	0.418	0.535	0.669
1.255	29.3	51	27.76	34.00	43.57	54.40	0.348	0.426	0.547	0.683
1.260	29.7	52	28.22	34.57	44.30	55.31	0.356	0.435	0.558	0.697
1.265	30.2	53	28.69	35.14	45.03	56.22	0.363	0.444	0.570	0.711
1.270	30.6	54	29.15	35.71	45.76	57.14	0.370	0.454	0.582	0.725
1.275	31.1	55	29.62	36.29	46.50	58.06	0.377	0.462	0.593	0.740
1.280	31.5	56	30.10	36.87	47.24	58.99	0.385	0.472	0.605	0.755
1.285	32.0	57	30.57	37.45	47.99	59.92	0.393	0.481	0.617	0.770
1.290	32.4	58	31.04	38.03	48.73	60.85	0.400	0.490	0.629	0.785
1.295	32.8	59	31.52	38.61	49.47	61.78	0.408	0.500	0.641	0.800
1.300	33.3	60	32.00	39.19	50.21	62.70	0.416	0.510	0.653	0.815
1.305	33.7	61	32.46	39.77	50.96	63.63	0.424	0.519	0.665	0.830
1.310	34.2	62	32.94	40.35	51.71	64.56	0.432	0.529	0.677	0.845
1.315	34.6	63	33.41	40.93	52.45	65.45	0.439	0.538	0.689	0.860
1.320	35.0	64	33.88	41.50	53.18	66.40	0.447	0.548	0.702	0.876
1.325	35.4	65	34.35	42.08	53.92	67.33	0.455	0.557	0.714	0.892
1.330	35.8	66	34.80	42.66	54.67	68.26	0.462	0.567	0.727	0.908
1.335	36.2	67	35.27	43.20	55.36	69.12	0.471	0.577	0.739	0.923
1.340	36.6	68	35.71	43.74	56.05	69.98	0.479	0.586	0.751	0.938

## Specific Gravity of Sulphuric Acid Solutions—Continued.

Sp. Gr. at 15° (in vacuo).	Degrees Baumé.	Degrees Twaddell.	100 parts by weight of chemically pure Acid contain per cent.				1 Litre of chemically pure Acid contains kilograms of			
			SO <sub>3</sub> .	H <sub>2</sub> SO <sub>4</sub> .	Acid of 142° Tw.	Acid of 106° Tw.	SO <sub>3</sub> .	H <sub>2</sub> SO <sub>4</sub> .	Acid of 142° Tw.	Acid of 106° Tw.
1.345	37.0	69	36.14	44.28	56.74	70.85	0.486	0.596	0.763	0.953
1.350	37.4	70	36.58	44.82	57.43	71.71	0.494	0.605	0.775	0.968
1.355	37.8	71	37.02	45.35	58.11	72.56	0.502	0.614	0.787	0.983
1.360	38.2	72	37.45	45.88	58.79	73.41	0.509	0.624	0.800	0.998
1.365	38.6	73	37.89	46.41	59.48	74.26	0.517	0.633	0.812	1.014
1.370	39.0	74	38.32	46.94	60.15	75.10	0.525	0.643	0.824	1.029
1.375	39.4	75	38.75	47.47	60.83	75.95	0.533	0.653	0.836	1.044
1.380	39.8	76	39.18	48.00	61.51	76.80	0.541	0.662	0.849	1.060
1.385	40.1	77	39.62	48.53	62.19	77.65	0.549	0.672	0.861	1.075
1.390	40.5	78	40.05	49.06	62.87	78.50	0.557	0.682	0.873	1.091
1.395	40.8	79	40.48	49.59	63.55	79.34	0.564	0.692	0.886	1.107
1.400	41.2	80	40.91	50.11	64.21	80.18	0.573	0.702	0.899	1.123
1.405	41.6	81	41.33	50.63	64.88	81.01	0.581	0.711	0.912	1.138
1.410	42.0	82	41.76	51.15	65.55	81.86	0.589	0.721	0.924	1.154
1.415	42.3	83	42.17	51.66	66.21	82.66	0.597	0.730	0.937	1.170
1.420	42.7	84	42.57	52.15	66.82	83.44	0.604	0.740	0.949	1.185
1.425	43.1	85	42.96	52.63	67.44	84.21	0.612	0.750	0.961	1.200
1.430	43.4	86	43.36	53.11	68.06	84.98	0.620	0.759	0.973	1.215
1.435	43.8	87	43.75	53.59	68.68	85.74	0.628	0.769	0.986	1.230
1.440	44.1	88	44.14	54.07	69.29	86.51	0.636	0.779	0.998	1.246
1.445	44.4	89	44.53	54.55	69.90	87.28	0.643	0.789	1.010	1.261
1.450	44.8	90	44.92	55.03	70.52	88.05	0.651	0.798	1.023	1.277
1.455	45.1	91	45.31	55.50	71.12	88.80	0.659	0.808	1.035	1.292
1.460	45.4	92	45.69	55.97	71.72	89.55	0.667	0.817	1.047	1.307
1.465	45.8	93	46.07	56.43	72.31	90.29	0.675	0.827	1.059	1.323
1.470	46.1	94	46.45	56.90	72.91	91.04	0.683	0.837	1.072	1.338
1.475	46.4	95	46.83	57.37	73.51	91.79	0.692	0.846	1.084	1.354
1.480	46.8	96	47.21	57.83	74.10	92.53	0.699	0.856	1.097	1.370
1.485	47.1	97	47.57	58.28	74.68	93.25	0.707	0.865	1.109	1.385
1.490	47.4	98	47.95	58.74	75.27	93.98	0.715	0.876	1.122	1.400
1.495	47.8	99	48.34	59.22	75.88	94.75	0.723	0.885	1.134	1.417
1.500	48.1	100	48.73	59.70	76.50	95.52	0.731	0.896	1.147	1.433
1.505	48.4	101	49.12	60.18	77.12	96.29	0.739	0.906	1.160	1.449
1.510	48.7	102	49.51	60.65	77.72	97.04	0.748	0.916	1.174	1.465
1.515	49.0	103	49.89	61.12	78.32	97.79	0.756	0.926	1.187	1.481
1.520	49.4	104	50.28	61.59	78.93	98.54	0.764	0.936	1.199	1.498
1.525	49.7	105	50.66	62.06	79.52	99.30	0.773	0.946	1.213	1.514
1.530	50.0	106	51.04	62.53	80.13	100.05	0.781	0.957	1.226	1.531
1.535	50.3	107	51.43	63.00	80.73	100.80	0.789	0.967	1.239	1.547
1.540	50.6	108	51.78	63.43	81.28	101.49	0.797	0.977	1.252	1.563
1.545	50.9	109	52.12	63.85	81.81	102.16	0.805	0.987	1.264	1.579
1.550	51.2	110	52.46	64.26	82.34	102.82	0.813	0.996	1.276	1.593
1.555	51.5	111	52.79	64.67	82.87	103.47	0.821	1.006	1.289	1.609
1.560	51.8	112	53.22	65.20	83.50	104.30	0.830	1.017	1.303	1.627
1.565	52.1	113	53.59	65.65	84.08	105.03	0.839	1.027	1.316	1.644
1.570	52.4	114	53.95	66.09	84.64	105.73	0.847	1.038	1.329	1.660
1.575	52.7	115	54.32	66.53	85.21	106.42	0.856	1.048	1.343	1.677
1.580	53.0	116	54.65	66.95	85.78	107.10	0.864	1.058	1.356	1.692
1.585	53.3	117	55.03	67.40	86.34	107.85	0.872	1.068	1.369	1.709
1.590	53.6	118	55.37	67.83	86.88	108.52	0.880	1.078	1.382	1.726
1.595	53.9	119	55.73	68.26	87.44	109.21	0.889	1.089	1.395	1.742
1.600	54.1	120	56.09	68.70	88.00	109.92	0.897	1.099	1.409	1.759
1.605	54.4	121	56.44	69.13	88.55	110.61	0.906	1.110	1.422	1.775



## APPENDIX

## Specific Gravity of Sulphuric Acid Solutions—Continued.

Sp. Gr. at 15° 4° (in vacuo).	Degrees Baumé.	Degrees Twaddell.	100 parts by weight of chemically pure Acid contain per cent.				1 Liter of chemically pure Acid contains kilograms of			
			SO <sub>3</sub> .	H <sub>2</sub> SO <sub>4</sub> .	Acid of 142° Tw.	Acid of 100° Tw.	SO <sub>3</sub> .	H <sub>2</sub> SO <sub>4</sub> .	Acid of 142° Tw.	Acid of 100° Tw.
1.610	54.7	122	56.79	69.56	89.10	111.30	0.914	1.120	1.435	1.792
1.615	55.0	123	57.15	70.00	89.66	112.00	0.923	1.131	1.449	1.810
1.620	55.2	124	57.49	70.42	90.20	112.68	0.931	1.141	1.462	1.825
1.625	55.5	125	57.84	70.85	90.74	113.35	0.940	1.151	1.473	1.842
1.630	55.8	126	58.18	71.27	91.29	114.02	0.948	1.162	1.489	1.859
1.635	56.0	127	58.53	71.70	91.83	114.71	0.957	1.172	1.502	1.875
1.640	56.3	128	58.88	72.12	92.38	115.40	0.966	1.182	1.516	1.892
1.645	56.6	129	59.22	72.55	92.92	116.06	0.975	1.193	1.529	1.909
1.650	56.9	130	59.57	72.96	93.45	116.72	0.983	1.204	1.543	1.926
1.655	57.1	131	59.92	73.40	94.02	117.44	0.992	1.215	1.557	1.944
1.660	57.4	132	60.26	73.81	94.54	118.11	1.000	1.225	1.570	1.960
1.665	57.7	133	60.61	74.24	95.08	118.77	1.009	1.230	1.584	1.977
1.670	57.9	134	60.95	74.66	95.62	119.36	1.017	1.246	1.598	1.995
1.675	58.2	135	61.29	75.08	96.16	120.11	1.027	1.259	1.611	2.012
1.680	58.4	136	61.63	75.50	96.69	120.50	1.035	1.268	1.625	2.029
1.685	58.7	137	61.93	75.94	97.21	121.38	1.043	1.278	1.638	2.046
1.690	58.9	138	62.29	76.38	97.77	122.08	1.053	1.289	1.652	2.064
1.695	59.2	139	62.64	76.76	98.32	122.77	1.062	1.301	1.667	2.082
1.700	59.5	140	63.00	77.17	98.89	123.47	1.071	1.312	1.681	2.100
1.705	59.7	141	63.35	77.60	99.44	124.16	1.080	1.323	1.696	2.117
1.710	60.0	142	63.70	78.04	100.00	124.86	1.089	1.334	1.710	2.136
1.715	60.2	143	64.07	78.48	100.56	125.57	1.099	1.346	1.725	2.154
1.720	60.4	144	64.43	78.92	101.13	126.27	1.108	1.357	1.739	2.172
1.725	60.6	145	64.78	79.36	101.69	126.98	1.118	1.369	1.754	2.191
1.730	60.9	146	65.14	79.80	102.25	127.68	1.127	1.381	1.769	2.209
1.735	61.1	147	65.50	80.24	102.82	128.38	1.136	1.392	1.784	2.228
1.740	61.4	148	65.86	80.68	103.38	129.09	1.146	1.404	1.799	2.247
1.745	61.6	149	66.22	81.12	103.95	129.79	1.156	1.416	1.814	2.265
1.750	61.8	150	66.58	81.56	104.52	130.49	1.165	1.427	1.829	2.284
1.755	62.1	151	66.94	82.00	105.08	131.20	1.175	1.439	1.845	2.303
1.760	62.3	152	67.30	82.44	105.64	131.90	1.185	1.451	1.859	2.321
1.765	62.5	153	67.76	83.01	106.31	132.80	1.196	1.465	1.877	2.344
1.770	62.8	154	68.17	83.51	106.91	133.61	1.207	1.478	1.894	2.365
1.775	63.0	155	68.60	84.02	107.62	134.43	1.218	1.491	1.911	2.386
1.780	63.2	156	68.98	84.50	108.27	135.20	1.228	1.504	1.928	2.407
1.785	63.5	157	69.47	85.10	109.05	136.16	1.240	1.519	1.947	2.432
1.790	63.7	158	69.96	85.70	109.82	137.14	1.252	1.534	1.965	2.455
1.795	64.0	159	70.45	86.30	110.58	138.08	1.265	1.549	1.983	2.479
1.800	64.2	160	70.96	86.92	111.32	139.06	1.277	1.565	2.003	2.503
1.805	64.4	161	71.50	87.60	112.25	140.16	1.291	1.581	2.026	2.530
1.810	64.6	162	72.08	88.30	113.15	141.28	1.305	1.598	2.048	2.558
1.815	64.8	163	72.96	89.16	114.21	142.65	1.322	1.618	2.074	2.589
1.820	65.0	164	73.51	90.05	115.33	144.08	1.338	1.639	2.099	2.622
1.821	...	...	73.63	90.20	115.59	144.32	1.341	1.643	2.104	2.628
1.822	65.1	...	73.80	90.40	115.84	144.64	1.345	1.647	2.110	2.635
1.823	...	...	73.96	90.60	116.10	144.96	1.348	1.651	2.116	2.648
1.824	65.2	...	74.12	90.80	116.35	145.28	1.352	1.656	2.122	2.650
1.825	...	165	74.29	91.00	116.61	145.60	1.356	1.661	2.128	2.657
1.826	65.3	...	74.49	91.25	116.93	146.00	1.360	1.666	2.135	2.666
1.827	...	...	74.69	91.50	117.25	146.40	1.364	1.671	2.142	2.675
1.828	65.4	...	74.86	91.70	117.51	146.72	1.368	1.676	2.148	2.682
1.829	...	...	75.03	91.90	117.76	147.04	1.372	1.681	2.154	2.689
1.830	...	166	75.19	92.10	118.02	147.36	1.376	1.685	2.159	2.696

## Specific Gravity of Sulphuric Acid Solutions—Continued.

Sp. Gr. at 15 °C. (in vacuo).	Degrees Baumé.	Degrees Twaddell.	100 parts by weight of chemically pure Acid contain per cent.				1 Litre of chemically pure Acid contains kilograms of			
			SO <sub>3</sub> .	H <sub>2</sub> SO <sub>4</sub> .	Acid of 142° Tw.	Acid of 106° Tw.	SO <sub>3</sub> .	H <sub>2</sub> SO <sub>4</sub> .	Acid of 142° Tw.	Acid of 106° Tw.
1·831	65·5	...	75·46	92·43	118·41	147·88	1·832	1·692	2·169	2·708
1·832	...	...	75·69	92·70	118·73	148·32	1·836	1·698	2·176	2·717
1·833	65·6	...	75·89	92·97	119·07	148·73	1·891	1·704	2·184	2·727
1·834	...	...	76·12	93·25	119·43	149·18	1·896	1·710	2·191	2·736
1·835	65·7	167	76·38	93·56	119·84	149·70	1·402	1·717	2·200	2·747
1·836	...	...	76·57	93·90	120·19	150·08	1·406	1·722	2·207	2·755
1·837	...	...	76·90	94·25	120·71	150·72	1·412	1·730	2·217	2·769
1·838	65·8	...	77·23	94·60	121·22	151·36	1·419	1·739	2·228	2·782
1·839	...	...	77·55	95·00	121·74	152·00	1·426	1·748	2·239	2·795
1·840	65·9	168	78·04	95·60	122·51	152·96	1·436	1·759	2·254	2·814
1·8405	...	...	78·33	95·95	122·96	153·52	1·451	1·765	2·262	2·825
1·8410	...	...	78·69	96·38	123·45	154·20	1·448	1·774	2·273	2·838
1·8415	...	...	79·47	97·35	124·69	155·74	1·463	1·792	2·296	2·867
1·8410	...	...	80·16	98·20	125·84	157·12	1·476	1·808	2·317	2·893
1·8405	...	...	80·48	98·52	126·18	157·62	1·481	1·814	2·325	2·903
1·8400	...	...	80·59	98·72	126·44	157·94	1·483	1·816	2·327	2·906
1·8395	...	...	80·63	98·77	126·50	158·00	1·484	1·817	2·328	2·907
1·8390	...	...	80·93	99·12	126·99	158·60	1·488	1·823	2·336	2·917
1·8385	...	...	81·08	99·31	127·35	158·90	1·490	1·826	2·339	2·921

# APPENDIX

TABLE XXVII. (*Part, p. 355.*)

Table showing the Influence of Temperature on the Specific Gravity of Sulphuric Acid.

*a.* Specific gravity at  $15\frac{3}{4}^{\circ}$  under  $t$ , changes in specific gravity at the temperature  $t$ .

	+0.015	+0.005	-0.005	-0.015	-0.025	-0.034	-0.044
1.840	16	5	5	16	26	37	47
1.820	16	5	5	16	27	37	47
1.800	17	5	5	16	27	37	47
1.780	17	5	5	16	26	36	47
1.760	16	5	5	16	25	35	45
1.740	16	5	5	15	25	35	44
1.720	15	5	5	14	24	33	43
1.700	15	5	5	14	24	33	42
1.680	15	5	5	14	23	32	41
1.660	14	5	5	14	23	32	40
1.640	14	5	4	14	22	31	40
1.620	14	4	4	13	22	31	39
1.600	14	4	4	13	22	30	39
1.580	14	4	4	13	21	30	38
1.560	13	4	4	13	21	30	38
1.540	13	4	4	13	21	29	37
1.520	13	4	4	12	21	29	37
1.500	13	4	4	12	20	28	36
1.480	13	4	4	12	20	28	36
1.460	12	4	4	12	20	28	35
1.440	12	4	4	12	19	27	35
1.420	12	4	4	12	19	27	34
1.400	12	4	4	11	19	27	34
1.380	11	4	4	11	19	26	34
1.360	11	4	4	11	19	26	33
1.340	11	3	4	11	18	26	33
1.320	11	3	3	11	18	25	32
1.300	11	3	3	11	18	25	32
1.280	11	3	3	10	17	24	31
1.260	10	3	3	10	17	23	30
1.240	10	3	3	10	16	23	29
1.220	9	3	3	9	15	22	28
1.200	8	3	3	8	14	20	27
1.180	8	2	2	8	14	19	25
1.160	7	2	2	7	13	18	24
1.140	6	2	2	7	12	17	23
1.120	5	2	2	6	10	16	21
1.100	3	1	1	5	9	14	20
1.080	2	1	1	4	8	13	18
1.060	2	1	1	4	7	12	17

TABLE XXVIII. (*T<sub>cat</sub>*, p. 357.)

Reduction of the Hydrometer Readings for Sulphuric Acid between 65° and 66° B.  
(164° and 168° Tw.) to 15°C.

The hydrometer reading is taken from the first vertical column, and the observed temperature from the top line. The reading which lies vertically below the observed temperature and on the line containing the observed specific gravity gives the specific gravity at 15°.

° B.	10°	11°	12°	13°	14°	15°	16°	17°	18°	19°	20°	21°	22°	23°	24°	25°	26°	27°	28°	29°	30°
65·00	64·80	64·84	64·88	64·92	64·96	65·00	65·04	65·08	65·12	65·16	65·20	65·24	65·28	65·32	65·36	65·40	65·44	65·48	65·52	65·56	65·60
65·10	64·90	64·94	64·98	65·02	65·06	65·10	65·14	65·18	65·22	65·26	65·30	65·34	65·38	65·42	65·46	65·50	65·54	65·58	65·62	65·66	65·70
65·20	65·00	65·04	65·08	65·12	65·16	65·20	65·24	65·28	65·32	65·36	65·40	65·44	65·48	65·52	65·56	65·60	65·64	65·68	65·72	65·76	65·80
65·30	65·10	65·14	65·18	65·22	65·26	65·30	65·34	65·38	65·42	65·46	65·50	65·54	65·58	65·62	65·66	65·70	65·74	65·78	65·82	65·86	65·90
65·40	65·20	65·24	65·28	65·32	65·36	65·40	65·44	65·48	65·52	65·56	65·60	65·64	65·68	65·72	65·76	65·80	65·84	65·88	65·92	65·96	66·00
65·50	65·30	65·34	65·38	65·42	65·46	65·50	65·54	65·58	65·62	65·66	65·70	65·74	65·78	65·82	65·86	65·90	65·94	65·98	66·02	66·06	66·10
65·60	65·40	65·44	65·48	65·52	65·56	65·60	65·64	65·68	65·72	65·76	65·80	65·84	65·88	65·92	65·96	66·00	66·04	66·08	66·12	66·16	66·20
65·70	65·50	65·54	65·58	65·62	65·66	65·70	65·74	65·78	65·82	65·86	65·90	65·94	65·98	66·02	66·06	66·10	66·14	66·18	66·22	66·26	66·30
65·80	65·60	65·64	65·68	65·72	65·76	65·80	65·84	65·88	65·92	65·96	66·00	66·04	66·08	66·12	66·16	66·20	66·24	66·28	66·32	66·36	66·40
65·90	65·70	65·74	65·78	65·82	65·86	65·90	65·94	65·98	66·02	66·06	66·10	66·14	66·18	66·22	66·26	66·30	66·34	66·38	66·42	66·46	66·50
66·00	65·80	65·84	65·88	65·92	65·96	66·00	66·04	66·08	66·12	66·16	66·20	66·24	66·28	66·32	66·36	66·40	66·44	66·48	66·52	66·56	66·60

TABLE XXIX. (*Text*, p. 358.)

## Melting Points of Sulphuric Acid. Knietsch.

Enlarged by Lunge by the addition of the corresponding percentage of  $H_2SO_4$ . The melting points given in the table are the temperatures, which remain constant during the period of complete crystallisation; that is, from the temperature at which crystals begin to appear in the cooled acid until the stage when the mass becomes solid after removal from the freezing mixture.

Sulphuric Acid								
Total $SO_3$ per cent.	$H_2SO_4$ per cent.	Melting Point, $^{\circ}C$ .	Total $SO_3$ per cent.	$H_2SO_4$ per cent.	Melting Point, $^{\circ}C$ .	Total $SO_3$ per cent.	$H_2SO_4$ per cent.	Melting Point, $^{\circ}C$ .
1	1.22	- 0.8	23	23.17	- 40.1	80	98.00	+ 3.0
2	2.45	- 1.0	...	...	Under	81	99.25	+ 7.0
3	3.67	- 1.7	...	...	- 40.0	81.63	100.00	+ 10.0
4	4.90	- 2.0	61	74.72	- 40.0	82	...	+ 8.2
5	6.12	- 2.7	62	75.95	- 20.0	83	...	- 0.8
6	7.35	- 3.6	63	77.17	- 11.5	84	...	+ 9.2
7	8.57	- 4.4	64	78.40	- 4.8	85	...	+ 11.0
8	9.80	- 5.3	65	79.62	- 4.2	86	...	- 2.2
9	11.02	- 6.0	66	80.85	+ 1.2	87	...	+ 13.5
10	12.25	- 6.7	67	82.07	+ 8.0	88	...	+ 26.0
11	13.47	- 7.2	68	83.39	+ 8.0	89	...	+ 34.2
12	14.70	- 7.9	69	84.52	+ 7.0	90	...	+ 34.2
13	15.92	- 8.2	70	85.75	+ 4.0	91	...	+ 25.8
14	17.15	- 9.0	71	86.97	- 1.0	92	...	+ 14.2
15	18.37	- 9.3	72	88.20	- 7.2	93	...	+ 0.8
16	19.60	- 9.8	73	89.42	- 16.2	94	...	+ 4.5
17	20.82	- 11.4	74	90.65	- 25.0	95	...	+ 14.8
18	22.05	- 13.2	75	91.87	- 34.0	96	...	+ 20.3
19	23.27	- 15.2	76*	93.10	- 32.0	97	...	+ 29.2
20	24.50	- 17.1	77*	94.33	- 23.2	98	...	+ 33.8
21	25.72	- 22.5	78*	95.05	- 16.5	99	...	+ 36.0
22	26.95	- 31.0	79	96.77	- 5.2	100	...	+ 40.0

\* So-called 160° Tw.

TABLE XXX. (*Text*, p. 358.)

## Boiling Points of Sulphuric Acid.

Per cent. $H_2SO_4$ .	Specific Gravity.	Degrees Baumé.	Boiling Point, $^{\circ}C$ .	Per cent. $H_2SO_4$ .	Specific Gravity.	Degrees Baumé.	Boiling Point, $^{\circ}C$ .	Per cent. $H_2SO_4$ .	Specific Gravity.	Degrees Baumé.	Boiling Point, $^{\circ}C$ .
5	1.031	4.2	101	56	1.459	45.4	183	82	1.758	32.2	218.5
10	1.069	9.2	102	60	1.503	48.3	141.5	84	1.773	33.0	227
15	1.107	13.9	103.5	62.5	1.530	50.0	147	86	1.791	34.8	238.5
20	1.147	18.5	105	65	1.557	51.6	153.5	88	1.807	34.4	251.5
25	1.184	22.4	106.5	67.5	1.585	53.3	161	90	1.818	35.0	262.5
30	1.224	26.4	108	70	1.615	55.0	170	91	1.824	35.3	268
35	1.265	30.2	110	72	1.639	56.3	174.5	92	1.830	35.45	274.5
40	1.307	33.9	114	74	1.661	57.4	180.5	93	1.834	35.65	281.5
45	1.352	37.6	118.5	76	1.688	58.8	189	94	1.837	35.8	288.5
50	1.399	41.1	124	78	1.710	60.0	199	95	1.840	35.9	295
53	1.428	43.3	128.5	80	1.733	61.0	207	...	...	...	...

TABLE XXXI. (*Text*, p. 386.)

Specific Gravity of Fuming Sulphuric Acid at 35° C.  
Knietzsch.

Total SO <sub>3</sub> per cent.	Free SO <sub>3</sub> per cent.	Specific Gravity.	Total SO <sub>3</sub> per cent.	Free SO <sub>3</sub> per cent.	Specific Gravity.
81.63	0	1.8186	91.18	52	1.9749
81.99	2	1.8270	91.55	54	1.9760
82.36	4	1.8360	91.91	56	1.9772
82.73	6	1.8425	92.28	58	1.9754
83.09	8	1.8498	92.65	60	1.9738
83.46	10	1.8565	93.02	62	1.9709
83.82	12	1.8627	93.38	64	1.9672
84.20	14	1.8692	93.75	66	1.9636
84.56	16	1.8756	94.11	68	1.9600
84.92	18	1.8830	94.48	70	1.9564
85.30	20	1.8919	94.85	72	1.9502
85.66	22	1.9020	95.21	74	1.9442
86.03	24	1.9092	95.58	76	1.9379
86.40	26	1.9158	95.95	78	1.9315
86.76	28	1.9220	96.32	80	1.9251
87.14	30	1.9280	96.69	82	1.9183
87.50	32	1.9338	97.05	84	1.9115
87.87	34	1.9405	97.42	86	1.9046
88.24	36	1.9474	97.78	88	1.8980
88.60	38	1.9534	98.16	90	1.8888
88.97	40	1.9584	98.53	92	1.8800
89.33	42	1.9612	98.90	94	1.8712
89.70	44	1.9643	99.26	96	1.8605
90.07	46	1.9672	99.63	98	1.8488
90.44	48	1.9702	100.00	100	1.8370
90.81	50	1.9733	...	...	...

TABLE XXXII. (Text, p. 394.)

Table for finding the Percentage of Free  $\text{SO}_3$  in Oleum from the Total  $\text{SO}_3$  as determined by Analysis. Knietzsch.

$\text{SO}_3$		$\text{SO}_3$		$\text{SO}_3$		$\text{SO}_3$		$\text{SO}_3$		$\text{SO}_3$	
Total.	Free.	Total.	Free.	Total.	Free.	Total.	Free.	Total.	Free.	Total.	Free.
81.63	0.0	84.7	16.7	87.8	33.6	90.9	50.5	94.0	67.3	97.0	83.7
81.7	0.4	84.8	17.2	87.9	34.1	91.0	51.0	94.1	67.9	97.1	84.2
81.8	0.9	84.9	17.8	88.0	34.7	91.1	51.6	94.2	68.4	97.2	84.8
81.9	1.5	85.0	18.3	88.1	35.2	91.2	52.1	94.3	69.0	97.3	85.3
82.0	2.0	85.1	18.9	88.2	35.8	91.3	52.6	94.4	69.5	97.4	85.8
82.1	2.6	85.2	19.4	88.3	36.3	91.4	53.2	94.5	70.1	97.5	86.4
82.2	3.1	85.3	20.0	88.4	36.8	91.5	53.7	94.6	70.6	97.6	86.9
82.3	3.6	85.4	20.5	88.5	37.4	91.6	54.3	94.7	71.2	97.7	87.5
82.4	4.2	85.5	21.0	88.6	37.9	91.7	54.8	94.8	71.7	97.8	88.0
82.5	4.7	85.6	21.6	88.7	38.5	91.8	55.4	94.9	72.2	97.9	88.6
82.6	5.3	85.7	22.2	88.8	39.0	91.9	55.9	95.0	72.8	98.0	89.1
82.7	5.8	85.8	22.7	88.9	39.6	92.0	56.4	95.1	73.3	98.1	89.7
82.8	6.4	85.9	23.2	89.0	40.1	92.1	57.0	95.2	73.9	98.2	90.2
82.9	6.9	86.0	23.8	89.1	40.6	92.2	57.5	95.3	74.4	98.3	90.7
83.0	7.5	86.1	24.3	89.2	41.2	92.3	58.1	95.4	75.0	98.4	91.3
83.1	8.0	86.2	24.9	89.3	41.7	92.4	58.6	95.5	75.5	98.5	91.8
83.2	8.5	86.3	25.4	89.4	42.3	92.5	59.2	95.6	76.1	98.6	92.4
83.3	9.1	86.4	26.0	89.5	42.8	92.6	59.7	95.7	76.6	98.7	92.9
83.4	9.6	86.5	26.5	89.6	43.4	92.7	60.3	95.8	77.1	98.8	93.5
83.5	10.2	86.6	27.0	89.7	43.9	92.8	60.8	95.9	77.7	98.9	94.0
83.6	10.7	86.7	27.6	89.8	44.5	92.9	61.3	96.0	78.3	99.0	94.6
83.7	11.3	86.8	28.1	89.9	45.0	93.0	61.9	96.1	78.8	99.1	95.1
83.8	11.8	86.9	28.7	90.0	45.6	93.1	62.4	96.2	79.3	99.2	95.6
83.9	12.3	87.0	29.2	90.1	46.1	93.2	63.0	96.3	79.9	99.3	96.2
84.0	12.9	87.1	29.8	90.2	46.6	93.3	63.5	96.4	80.4	99.4	96.7
84.1	13.4	87.2	30.3	90.3	47.2	93.4	64.1	96.5	81.0	99.5	97.3
84.2	14.0	87.3	30.9	90.4	47.7	93.5	64.6	96.6	81.5	99.6	97.8
84.3	14.5	87.4	31.4	90.5	48.3	93.6	65.2	96.7	82.0	99.7	98.4
84.4	15.1	87.5	31.9	90.6	48.8	93.7	65.7	96.8	82.6	99.8	98.9
84.5	15.6	87.6	32.5	90.7	49.4	93.8	66.2	96.9	83.1	99.9	99.5
84.6	16.2	87.7	33.0	90.8	49.9	93.9	66.8	...	...	...	...

TABLE XXXIII. (*Text*, p. 395.)

Table for finding the Percentage of  $\text{SO}_3$  in Oleum from the Total Acidity, calculated as  $\text{H}_2\text{SO}_4$ . Grünhut.

Whole numbers.			*	Hundredth Parts.									
10	11	12		0	1	2	3	4	5	6	7	8	9
0	44.428	88.857	0	0	0.044	0.089	0.133	0.178	0.222	0.267	0.311	0.355	0.400
4.443	48.871	93.300	1	0.444	0.489	0.533	0.578	0.622	0.666	0.711	0.755	0.800	0.844
8.886	53.314	97.743	2	0.889	0.933	0.977	1.022	1.066	1.111	1.155	1.200	1.244	1.288
13.329	57.757	...	3	1.333	1.377	1.422	1.466	1.511	1.555	1.599	1.644	1.688	1.733
17.771	62.200	...	4	1.777	1.822	1.866	1.910	1.955	1.999	2.044	2.088	2.133	2.177
22.214	66.643	...	5	2.221	2.266	2.310	2.355	2.399	2.444	2.488	2.532	2.577	2.621
26.657	71.085	...	6	2.666	2.710	2.755	2.799	2.843	2.888	2.932	2.977	3.021	3.066
31.100	75.528	...	7	3.110	3.154	3.199	3.243	3.288	3.332	3.377	3.421	3.465	3.510
35.543	79.971	...	8	3.554	3.599	3.643	3.688	3.732	3.776	3.821	3.865	3.909	3.954
39.986	84.414	...	9	3.999	4.043	4.087	4.132	4.176	4.221	4.265	4.310	4.354	4.398

TABLE XXXIV. (*Text*, p. 397.)

Specific Gravity of Solutions of Sodium Chloride.

Specific Gravity.	Percentage NaCl.	Specific Gravity.	Percentage NaCl.	Specific Gravity.	Percentage NaCl.
1.00725	1	1.07335	10	1.14315	19
1.01450	2	1.08097	11	1.15107	20
1.02174	3	1.08859	12	1.15931	21
1.02899	4	1.09622	13	1.16755	22
1.03624	5	1.10384	14	1.17580	23
1.04366	6	1.11146	15	1.18404	24
1.05108	7	1.11938	16	1.19228	25
1.05851	8	1.12730	17	1.20098	26
1.06593	9	1.13523	18	1.20433	26.395



TABLE XXXV. (*Terl*, p. 412.)

Specific Gravity of Hydrochloric Acid Solutions at 15° C., compared with Water at 4°, and reduced to vacuum.

Lunge and Marchlewski.

Degrees Twaddell.	Specific Gravity at 15° 4° (in vacuo).	100 parts by weight correspond to parts by weight of			1 litre contains grms. HCl.	1 cubic foot contains lbs. HCl
		HCl.	Acid of Sp. Gr. 1.1425 = 28° 5 Tw.	Acid of Sp. Gr. 1.152 = 30° 4 Tw.		
0	1.000	0.16	0.57	0.53	1.6	0.10
1	1.005	1.15	4.08	3.84	12	0.75
2	1.010	2.14	7.60	7.14	22	1.37
3	1.015	3.12	11.80	10.41	32	1.99
4	1.020	4.13	14.67	13.79	42	2.62
5	1.025	5.15	18.30	17.19	53	3.30
6	1.030	6.15	21.85	20.53	64	3.99
7	1.035	7.15	25.40	23.87	74	4.61
8	1.040	8.16	28.99	27.24	85	5.30
9	1.045	9.16	32.55	30.58	96	5.98
10	1.050	10.17	36.14	33.95	107	6.67
11	1.055	11.18	39.73	37.33	118	7.35
12	1.060	12.19	43.32	40.70	129	8.04
13	1.065	13.19	46.87	44.04	141	8.79
14	1.070	14.17	50.35	47.31	152	9.48
15	1.075	15.16	53.87	50.62	163	10.16
16	1.080	16.15	57.39	53.92	174	10.85
17	1.085	17.13	60.87	57.19	186	11.59
18	1.090	18.11	64.35	60.47	197	12.28
19	1.095	19.06	67.73	63.64	209	13.03
20	1.100	20.01	71.11	66.81	220	13.71
21	1.105	20.97	74.52	70.01	232	14.46
22	1.110	21.92	77.89	73.19	243	15.15
23	1.115	22.86	81.23	76.32	255	15.90
24	1.120	23.82	84.64	79.53	267	16.65
25	1.125	24.78	88.06	82.74	278	17.33
26	1.130	25.75	91.50	85.97	291	18.14
27	1.135	26.70	94.88	89.15	303	18.89
28	1.140	27.66	98.29	92.35	315	19.64
29	1.145	28.61	101.67	95.52	328	20.45
30	1.150	29.57	105.08	98.73	340	21.20
31	1.155	30.55	108.58	102.00	353	22.01
32	1.160	31.52	112.01	105.24	366	22.82
33	1.165	32.49	115.46	108.48	379	23.63
34	1.170	33.46	118.91	111.71	392	24.44
35	1.175	34.42	122.32	114.92	404	25.19
36	1.180	35.39	125.76	118.16	418	26.06
37	1.185	36.31	129.03	121.23	430	26.81
38	1.190	37.23	132.30	124.30	443	27.62
39	1.195	38.16	135.61	127.41	456	28.43
40	1.200	39.11	138.98	130.58	469	29.24

TABLE XXXVI. (*Text*, p. 447.)

Specific Gravity of Solutions of Sodium Carbonate  
at 15° C. = 60° F.

Specific Gravity.	Percentage by Weight.		Kilos per 1 cubic metre.	
	Na <sub>2</sub> CO <sub>3</sub> .	Na <sub>2</sub> CO <sub>3</sub> 10H <sub>2</sub> O.	Na <sub>2</sub> CO <sub>3</sub>	Na <sub>2</sub> CO <sub>3</sub> 10H <sub>2</sub> O.
1.007	0.67	1.807	6.8	18.2
1.014	1.33	3.587	13.5	36.4
1.022	2.09	5.637	21.4	57.6
1.029	2.76	7.444	28.4	76.6
1.036	3.43	9.251	35.5	95.8
1.045	4.29	11.570	44.8	120.9
1.052	4.94	13.323	52.0	140.2
1.060	5.71	15.400	60.5	163.2
1.067	6.37	17.180	68.0	183.3
1.075	7.12	19.203	76.5	206.4
1.083	7.88	21.252	85.3	230.2
1.091	8.62	23.248	94.0	253.6
1.100	9.43	25.432	103.7	279.8
1.108	10.19	27.482	112.9	304.5
1.116	10.95	29.532	122.2	329.6
1.125	11.81	31.851	132.9	358.3
1.134	12.61	34.009	143.0	385.7
1.142	13.16	35.493	150.3	405.3
1.152	14.24	38.405	164.1	442.4

TABLE XXXVII. (*Text*, p. 448.)

Specific Gravity of Solutions of Sodium Carbonate in degrees  
Twaddell at 15° C. = 60° F.

Twaddell.	Percentage by Weight.		Lbs. per 1 cubic foot of solution.	
	Na <sub>2</sub> O.	Na <sub>2</sub> CO <sub>3</sub>	Na <sub>2</sub> O.	Na <sub>2</sub> CO <sub>3</sub> .
1	0.28	0.47	0.172	0.294
2	0.56	0.95	0.350	0.598
3	0.84	1.42	0.525	0.898
4	1.11	1.90	0.707	1.209
5	1.39	2.38	0.889	1.521
6	1.67	2.85	1.070	1.880
7	1.95	3.33	1.257	2.149
8	2.22	3.80	1.441	2.464
9	2.50	4.28	1.631	2.788
10	2.78	4.76	1.852	3.116
11	3.06	5.23	2.012	3.440
12	3.34	5.71	2.206	3.772
13	3.61	6.17	2.396	4.097
14	3.88	6.64	2.591	4.430
15	4.16	7.10	2.783	4.759
16	4.42	7.57	2.981	5.098
17	4.70	8.04	3.181	5.439
18	4.97	8.51	3.382	5.783
19	5.24	8.97	3.582	6.125
20	5.52	9.43	3.783	6.468
21	5.79	9.90	3.989	6.821
22	6.06	10.37	4.197	7.177
23	6.33	10.83	4.403	7.529
24	6.61	11.30	4.615	7.891
25	6.88	11.76	4.825	8.249
26	7.15	12.23	5.040	8.617
27	7.42	12.70	5.256	8.988
28	7.70	13.16	5.465	9.354
29	7.97	13.63	5.691	9.718
30	8.24	14.09	5.908	10.103

TABLE XXXVIII. (Text, p. 449.)

Specific Gravity of Concentrated Solutions of Sodium Carbonate  
at 30° C. = 86° F.

Specific Gravity at 80°.	Degrees Twaddell.	100-lbs. contain lbs.		1 litre contains grms.	
		Na <sub>2</sub> CO <sub>3</sub> .	Na <sub>2</sub> CO <sub>3</sub> , 10 aq.	Na <sub>2</sub> CO <sub>3</sub> .	Na <sub>2</sub> CO <sub>3</sub> , 10 aq.
1.310	62	28.13	75.91	368.5	994.5
1.300	60	27.30	73.67	354.9	957.4
1.290	58	26.46	71.40	341.3	921.0
1.280	56	25.62	69.11	327.9	884.7
1.270	54	24.78	66.86	314.7	849.2
1.260	52	23.93	64.59	301.5	813.2
1.250	50	23.08	62.15	288.5	778.5
1.240	48	22.21	59.94	275.4	743.0
1.230	46	21.33	57.55	262.3	707.8
1.220	44	20.47	55.29	249.7	673.8
1.210	42	19.61	52.91	237.3	640.3
1.200	40	18.76	50.62	225.1	607.4
1.190	38	17.90	48.31	214.0	577.5
1.180	36	17.04	45.97	201.1	542.6
1.170	34	16.18	43.38	189.3	510.9
1.160	32	15.32	41.34	177.7	479.5
1.150	30	14.47	39.04	164.4	449.0
1.140	28	13.62	36.75	155.3	419.0

TABLE XXXIX. (Text, p. 449.)

Influence of Temperature on the Specific Gravity of Sodium Carbonate Solutions.

(Approximate mean values for  $\pm 1^\circ$  C.)

For Temperatures from					For Specific Gravities	
0° to 30°.	30° to 40°.	40° to 50°.	50° to 70°.	70° to 100°.	From	To
0.0002	0.0004	0.0004	0.0005	0.0005	1.010	1.050
0.0003	0.0004	0.0004	0.0006	0.0005	1.060	1.070
0.0004	0.0004	0.0004	0.0006	0.0006	1.080	1.110
0.0004	0.0004	0.0005	0.0006	0.0006	1.120	1.170
0.0004	0.0004	0.0006	0.0007	0.0007	1.180	1.200
0.0005	0.0004	0.0005	0.0007	0.0007	1.210	1.240
...	0.0005	0.0005	0.0007	0.0007	1.241	1.252
...	0.0005	0.0005	0.0006	0.0008	1.263	1.285

TABLE XL. (Text, p. 452.)

English, German, and French Commercial Alkalimetric Degrees.

Real Soda, Na <sub>2</sub> O (Gay-Lussac Degrees).	English or Newcastle, Degrees.	German Degrees, Na <sub>2</sub> CO <sub>3</sub> .	French Degrees (Descroizilles).	Real Soda, Na <sub>2</sub> O (Gay-Lussac Degrees).	English or Newcastle Degrees.	German Degrees, Na <sub>2</sub> CO <sub>3</sub> .	French Degrees (Descroizilles).	Real Soda, Na <sub>2</sub> O (Gay-Lussac Degrees).	English or Newcastle Degrees.	German Degrees, Na <sub>2</sub> CO <sub>3</sub> .	French Degrees (Descroizilles).
0.5	0.51	0.85	0.79	26.5	26.85	45.31	41.38	52.5	53.10	89.76	82.98
1	1.01	1.81	1.58	27	27.35	46.17	42.07	53	53.70	90.61	83.77
1.5	1.52	2.56	2.37	27.5	27.86	47.02	43.46	53.5	54.20	91.47	84.56
2	2.03	3.42	3.16	28	28.36	47.88	44.25	54	54.71	92.32	85.35
2.5	2.54	4.27	3.95	28.5	28.87	48.73	45.04	54.5	55.22	93.18	86.14
3	3.04	5.13	4.74	29	29.38	49.59	45.83	55	55.72	94.03	86.93
3.5	3.55	5.98	5.53	29.5	29.89	50.44	46.62	55.5	56.23	94.89	87.72
4	4.05	6.84	6.32	30	30.39	51.29	47.42	56	56.74	95.74	88.52
4.5	4.56	7.69	7.11	30.5	30.90	52.14	48.21	56.5	57.24	96.60	89.31
5	5.06	8.55	7.90	31	31.41	53.00	49.00	57	57.75	97.45	90.10
5.5	5.57	9.40	8.69	31.5	31.91	53.85	49.79	57.5	58.26	98.31	90.89
6	6.08	10.26	9.48	32	32.42	54.71	50.88	58	58.76	99.16	91.68
6.5	6.59	11.11	10.27	32.5	32.92	55.56	51.37	58.5	59.27	100.02	92.47
7	7.09	11.97	11.06	33	33.43	56.42	52.16	59	59.77	100.87	93.26
7.5	7.60	12.82	11.85	33.5	33.94	57.27	52.95	59.5	60.28	101.73	94.05
8	8.10	13.68	12.64	34	34.44	58.13	53.74	60	60.79	102.58	94.84
8.5	8.61	14.53	13.43	34.5	34.95	58.98	54.53	60.5	61.30	103.44	95.63
9	9.12	15.39	14.22	35	35.46	59.84	55.32	61	61.80	104.30	96.42
9.5	9.63	16.24	15.01	35.5	35.96	60.69	56.11	61.5	62.31	105.15	97.21
10	10.13	17.10	15.81	36	36.47	61.55	56.90	62	62.82	106.01	98.00
10.5	10.64	17.95	16.60	36.5	36.98	62.40	57.69	62.5	63.32	106.86	98.79
11	11.14	18.81	17.39	37	37.48	63.26	58.48	63	63.83	107.72	99.58
11.5	11.65	19.66	18.18	37.5	37.98	64.11	59.27	63.5	64.33	108.57	100.37
12	12.17	20.52	18.97	38	38.50	64.97	60.06	64	64.84	109.43	101.16
12.5	12.68	21.37	19.76	38.5	39.00	65.82	60.85	64.5	65.35	110.28	101.95
13	13.17	22.23	20.55	39	39.51	66.68	61.64	65	65.85	111.14	102.74
13.5	13.68	23.08	21.34	39.5	40.02	67.53	62.43	65.5	66.36	111.99	103.53
14	14.18	23.94	22.13	40	40.52	68.39	63.22	66	66.87	112.85	104.32
14.5	14.69	24.79	22.92	40.5	41.03	69.24	64.01	66.5	67.37	113.70	105.11
15	15.19	25.65	23.71	41	41.54	70.10	64.81	67	67.88	114.56	105.90
15.5	15.70	26.50	24.50	41.5	42.04	70.95	65.60	67.5	68.39	115.41	106.69
16	16.21	27.36	25.29	42	42.55	71.81	66.39	68	68.89	116.27	107.48
16.5	16.73	28.21	26.08	42.5	43.06	72.66	67.18	68.5	69.40	117.12	108.27
17	17.22	29.07	26.87	43	43.57	73.52	67.97	69	69.91	117.98	109.06
17.5	17.73	29.92	27.67	43.5	44.07	74.37	68.76	69.5	70.41	118.83	109.85
18	18.23	30.78	28.45	44	44.58	75.23	69.55	70	70.92	119.69	110.64
18.5	18.74	31.63	29.24	44.5	45.08	76.08	70.34	70.5	71.43	120.53	111.43
19	19.25	32.49	30.02	45	45.59	76.94	71.13	71	71.93	121.39	112.23
19.5	19.76	33.34	30.82	45.5	46.10	77.80	71.92	71.5	72.44	122.24	113.02
20	20.26	34.20	31.61	46	46.60	78.66	72.71	72	72.95	123.10	113.81
20.5	20.77	35.05	32.40	46.5	47.11	79.51	73.50	72.5	73.45	123.95	114.60
21	21.27	35.91	33.19	47	47.62	80.37	74.29	73	73.96	124.81	115.39
21.5	21.78	36.76	33.98	47.5	48.12	81.22	75.08	73.5	74.47	125.66	116.18
22	22.29	37.62	34.77	48	48.63	82.07	75.87	74	74.97	126.52	116.97
22.5	22.80	38.47	35.56	48.5	49.14	82.93	76.66	74.5	75.48	127.37	117.76
23	23.30	39.33	36.35	49	49.64	83.78	77.45	75	75.99	128.23	118.55
23.5	23.81	40.18	37.14	49.5	50.15	84.64	78.24	75.5	76.49	129.08	119.34
24	24.31	41.04	37.93	50	50.66	85.48	79.03	76	77.00	129.94	120.13
24.5	24.82	41.89	38.72	50.5	51.16	86.34	79.82	76.5	77.51	130.79	120.92
25	25.32	42.75	39.51	51	51.67	87.19	80.61	77	78.01	131.65	121.71
25.5	25.83	43.60	40.30	51.5	52.18	88.05	81.40	77.5	78.52	132.50	122.50
26	26.34	44.46	41.09	52	52.68	88.90	82.19				

TABLE XLI. (*Text*, p. 464.)

Specific Gravity of Solutions of Sodium Hydroxide  
at 18° C. = 64° F.

NaOH per cent.	Specific Gravity.	NaOH per cent.	Specific Gravity.
0	0.99866	26	1.2860
1	1.01003	27	1.2968
2	1.02127	28	1.3076
3	1.03241	29	1.3184
4	1.04349	30	1.3290
5	1.05454	31	1.3396
6	1.06559	32	1.3502
7	1.07664	33	1.3605
8	1.08769	34	1.3708
9	1.09872	35	1.3811
10	1.10977	36	1.3913
11	1.12082	37	1.4014
12	1.13188	38	1.4115
13	1.14294	39	1.4215
14	1.15400	40	1.4314
15	1.16505	41	1.4411
16	1.17610	42	1.4508
17	1.18714	43	1.4604
18	1.19817	44	1.4699
19	1.20920	45	1.4794
20	1.22022	46	1.4890
21	1.23121	47	1.4985
22	1.24220	48	1.5080
23	1.25317	49	1.5174
24	1.26412	50	1.5268
25	1.27506		

TABLE XLII. (*Text*, p. 484.)

Specific Gravity and Composition of Milk of Lime  
at 15° C.

Degrees Twaddell.	Grams CaO per litre.	Lbs. CaO per cubic foot.	Degrees Twaddell.	Grams CaO per litre.	Lbs. CaO per cubic foot.
2	11.7	0.7	28	177	11.1
4	24.4	1.5	30	190	11.9
6	37.1	2.3	32	203	12.7
8	49.8	3.1	34	216	13.5
10	62.5	3.9	36	229	14.3
12	75.2	4.7	38	242	15.1
14	87.9	5.5	40	255	15.9
16	100	6.3	42	268	16.7
18	113	7.1	44	281	17.6
20	126	7.9	46	294	18.4
22	138	8.7	48	307	19.2
24	152	9.5	50	321	20.0
26	164	10.3	...	...	...

TABLE XLIII. (*Text, p. 499.*)

Table of the Percentage of Chlorine corresponding to  
French "Degrees."

French Degrees.	Per cent. Chlorine.	French Degrees.	Per cent. Chlorine.	French Degrees.	Per cent. Chlorine.	French Degrees.	Per cent. Chlorine.	French Degrees.	Per cent. Chlorine.
63	20.02	77	24.47	91	28.92	105	33.36	119	37.81
64	20.34	78	24.79	92	29.23	106	33.68	120	38.13
65	20.65	79	25.10	93	29.55	107	34.00	121	38.45
66	20.97	80	25.42	94	29.87	108	34.32	122	38.77
67	21.29	81	25.74	95	30.19	109	34.64	123	39.08
68	21.61	82	26.06	96	30.51	110	34.95	124	39.40
69	21.91	83	26.37	97	30.82	111	35.27	125	39.72
70	22.24	84	26.69	98	31.14	112	35.59	126	40.04
71	22.56	85	27.01	99	31.46	113	35.91	127	40.36
72	22.88	86	27.33	100	31.78	114	36.22	128	40.67
73	23.20	87	27.65	101	32.09	115	36.54	...	...
74	23.51	88	27.96	102	32.41	116	36.86	...	...
75	23.83	89	28.28	103	32.73	117	37.18	...	...
76	24.15	90	28.60	104	33.05	118	37.50	...	...

TABLE XLIV. (*Text, p. 500.*)

Specific Gravity of Bleach Solutions.

Specific Gravity at 15°.	Available Chlorine. Grms. per litre.	Specific Gravity at 15°.	Available Chlorine. Grms. per litre.	Specific Gravity at 15°.	Available Chlorine. Grms. per litre.
1.1155	71.79	1.0800	49.96	1.0350	20.44
1.1150	71.50	1.0750	45.70	1.0300	17.36
1.1105	68.40	1.0700	42.31	1.0250	14.47
1.1100	68.00	1.0650	39.10	1.0200	11.41
1.1060	65.83	1.0600	35.81	1.0150	8.48
1.1050	64.50	1.0550	32.68	1.0100	5.58
1.1000	61.50	1.0500	29.60	1.0050	2.71
1.0950	58.40	1.0450	26.62	1.0025	1.40
1.0900	55.18	1.0400	23.75	1.0000	Trace
1.0850	52.27	...	...	...	...

TABLE XLV.—Weight of 1 c.c. of Chlorine in Milligrams. Vanino. (*Text*, p. 508.)

For barometric pressures from 700 to 770 mm. and for temperatures from 10° to 25° C. For temperatures between 10° and 12°, deduct 1 mm. from the barometric pressure; between 13° and 14°, 2 mm.; between 20° and 25°, 3 mm.

Barometric Pressure. Mm.	10°	11°	12°	13°	14°	15°	16°	17°	18°	19°	20°	21°	22°	23°	24°	25°	Barometric Pressure. Mm.
700	2.777	2.765	2.752	2.740	2.728	2.715	2.702	2.690	2.677	2.664	2.651	2.637	2.624	2.610	2.597	2.583	700
702	2.785	2.773	2.761	2.748	2.736	2.723	2.710	2.698	2.684	2.671	2.658	2.645	2.632	2.618	2.604	2.590	702
704	2.793	2.781	2.769	2.756	2.744	2.731	2.718	2.705	2.692	2.679	2.666	2.653	2.639	2.626	2.612	2.598	704
706	2.801	2.789	2.777	2.764	2.752	2.739	2.726	2.713	2.700	2.687	2.674	2.660	2.647	2.633	2.619	2.606	706
708	2.809	2.797	2.785	2.772	2.760	2.747	2.734	2.721	2.708	2.695	2.682	2.668	2.655	2.641	2.627	2.613	708
710	2.817	2.805	2.793	2.780	2.767	2.755	2.742	2.729	2.716	2.702	2.689	2.676	2.663	2.649	2.635	2.621	710
712	2.826	2.813	2.801	2.788	2.775	2.763	2.750	2.737	2.724	2.710	2.697	2.684	2.670	2.656	2.643	2.629	712
714	2.834	2.821	2.808	2.796	2.783	2.770	2.757	2.745	2.732	2.718	2.705	2.691	2.678	2.664	2.650	2.636	714
716	2.842	2.829	2.816	2.804	2.791	2.778	2.765	2.753	2.739	2.726	2.713	2.699	2.686	2.672	2.658	2.644	716
718	2.850	2.837	2.824	2.812	2.799	2.786	2.773	2.760	2.747	2.734	2.720	2.707	2.693	2.679	2.665	2.651	718
720	2.858	2.845	2.832	2.820	2.807	2.794	2.781	2.768	2.755	2.741	2.728	2.715	2.701	2.687	2.673	2.659	720
722	2.866	2.853	2.840	2.828	2.815	2.802	2.789	2.776	2.763	2.749	2.736	2.723	2.709	2.695	2.681	2.667	722
724	2.874	2.861	2.848	2.836	2.823	2.810	2.797	2.784	2.771	2.757	2.744	2.730	2.716	2.703	2.689	2.674	724
726	2.882	2.869	2.856	2.844	2.831	2.818	2.805	2.792	2.779	2.765	2.751	2.738	2.724	2.710	2.696	2.682	726
728	2.890	2.877	2.864	2.852	2.839	2.826	2.813	2.799	2.786	2.773	2.759	2.746	2.732	2.718	2.704	2.690	728
730	2.898	2.885	2.872	2.860	2.847	2.834	2.821	2.807	2.794	2.780	2.767	2.754	2.740	2.726	2.712	2.697	730
732	2.906	2.893	2.880	2.868	2.854	2.841	2.828	2.815	2.802	2.788	2.775	2.761	2.747	2.733	2.719	2.705	732
734	2.914	2.901	2.888	2.876	2.862	2.849	2.836	2.823	2.809	2.796	2.782	2.769	2.755	2.741	2.727	2.712	734
736	2.922	2.909	2.896	2.883	2.870	2.857	2.844	2.831	2.817	2.804	2.790	2.777	2.763	2.749	2.734	2.720	736
738	2.930	2.917	2.904	2.891	2.878	2.865	2.852	2.839	2.825	2.812	2.798	2.784	2.770	2.756	2.742	2.728	738
740	2.938	2.925	2.912	2.899	2.886	2.873	2.860	2.847	2.833	2.819	2.806	2.792	2.778	2.764	2.750	2.735	740
742	2.946	2.933	2.920	2.907	2.894	2.881	2.868	2.855	2.841	2.827	2.814	2.800	2.786	2.772	2.758	2.743	742
744	2.954	2.941	2.928	2.915	2.902	2.889	2.876	2.862	2.849	2.835	2.821	2.808	2.794	2.780	2.765	2.751	744
746	2.962	2.949	2.936	2.923	2.910	2.897	2.884	2.870	2.857	2.843	2.829	2.815	2.801	2.787	2.773	2.758	746
748	2.970	2.957	2.944	2.931	2.918	2.905	2.891	2.878	2.864	2.851	2.837	2.823	2.809	2.795	2.780	2.766	748
750	2.978	2.965	2.952	2.939	2.926	2.913	2.899	2.886	2.872	2.858	2.845	2.831	2.817	2.802	2.788	2.774	750
752	2.986	2.973	2.960	2.947	2.934	2.921	2.907	2.894	2.880	2.866	2.852	2.838	2.824	2.810	2.796	2.781	752
754	2.994	2.981	2.968	2.955	2.942	2.929	2.915	2.901	2.888	2.874	2.860	2.846	2.832	2.818	2.804	2.789	754
756	3.002	2.989	2.976	2.963	2.950	2.936	2.923	2.909	2.896	2.882	2.868	2.854	2.840	2.825	2.811	2.796	756
758	3.010	2.997	2.984	2.971	2.957	2.944	2.931	2.917	2.904	2.890	2.876	2.862	2.848	2.833	2.819	2.804	758
760	3.018	3.005	2.992	2.979	2.965	2.952	2.939	2.925	2.911	2.897	2.884	2.869	2.855	2.841	2.827	2.812	760
762	3.026	3.013	3.000	2.987	2.973	2.960	2.947	2.933	2.919	2.905	2.891	2.877	2.863	2.849	2.834	2.819	762
764	3.035	3.021	3.008	2.995	2.981	2.968	2.954	2.941	2.927	2.913	2.899	2.885	2.871	2.856	2.842	2.827	764
766	3.043	3.029	3.016	3.003	2.989	2.976	2.962	2.949	2.935	2.921	2.907	2.893	2.878	2.864	2.849	2.835	766
768	3.051	3.037	3.024	3.011	2.997	2.984	2.970	2.957	2.943	2.929	2.914	2.900	2.886	2.872	2.857	2.842	768
770	3.059	3.045	3.033	3.019	3.005	2.991	2.978	2.965	2.951	2.937	2.922	2.908	2.894	2.879	2.865	2.850	770

Note.—This table is based on the value 3.16696 g. for the weight of 1 litre of chlorine, instead of on the correct value 3.210 g.; the figures are, therefore, 1.6 per cent. too low.



Pressure and Specific Gravity of Liquid Chlorine.  
R. Knietsch.<sup>1</sup>

Temperature. Degrees.	Pressure. <sup>o</sup>	Specific Gravity.	Mean Coefficient of Expansion.
-88	37.5 mm. Hg.	...	...
85	45.0 "	...	...
80	62.5 "	1.6602	0.001409
75	88.0 "	1.6490	
70	118 "	1.6382	
65	159 "	1.6273	
60	210 "	1.6167	
55	275 "	1.6055	
50	350 "	1.5945	
45	445 "	1.5830	
40	560 "	1.5720	
35	705 "	1.5589	
33.6	760 "	1.5575	0.001798
30	1.20 Atm.	1.5485	
25	1.50 "	1.5358	
20	1.84 "	1.5230	
15	2.23 "	1.5100	
10	2.63 "	1.4965	
5	3.14 "	1.4830	
0	3.66 "	1.4690	
+ 5	4.25 "	1.4548	
10	4.95 "	1.4405	0.001978
15	5.75 "	1.4273	0.002030
20	6.62 "	1.4118	0.002190
25	7.63 "	1.3984	
30	8.75 "	1.3815	0.002260
35	9.95 "	1.3683	
40	11.50 "	1.3510	0.002690
50	14.70 "	1.3170	
60	18.60 "	1.2830	0.003460
70	23.00 "	1.2430	
80	28.40 "	1.2000	...
90	34.50 "	...	...
100	41.70 "	...	...
110	50.80 "	...	...
120	60.40 "	...	...
130	71.60 "	...	...
146	93.50 "	Critical point.	...

TABLE XLVII. (*T<sub>cm</sub>*, p. 661.)  
 Determination of Calcium Carbonate in Limestone. Table of the Weight of Substance to be Weighed out  
 when 1 c.c. of carbon dioxide represents 1 per cent. of calcium carbonate, for barometric pressures of  
 from 720 to 770 mm. and for temperatures from 10° to 25° C.

Temp. °C	MILLIMETRES.													
	720	722	724	726	728	730	732	734	736	738	740	742	744	
10°	0.4033	0.4044	0.4055	0.4067	0.4078	0.4090	0.4101	0.4112	0.4124	0.4135	0.4146	0.4158	0.4170	
11	0.4015	0.4026	0.4038	0.4049	0.4060	0.4072	0.4083	0.4094	0.4106	0.4117	0.4128	0.4140	0.4151	
12	0.3997	0.4008	0.4020	0.4031	0.4042	0.4054	0.4065	0.4076	0.4087	0.4099	0.4110	0.4121	0.4132	
13	0.3979	0.3991	0.4002	0.4013	0.4024	0.4036	0.4047	0.4058	0.4069	0.4080	0.4092	0.4103	0.4114	
14	0.3961	0.3973	0.3984	0.3995	0.4006	0.4017	0.4029	0.4040	0.4051	0.4062	0.4073	0.4085	0.4096	
15	0.3943	0.3954	0.3965	0.3977	0.3988	0.3999	0.4010	0.4021	0.4032	0.4044	0.4055	0.4066	0.4077	
16	0.3925	0.3936	0.3947	0.3958	0.3969	0.3980	0.3992	0.4002	0.4014	0.4025	0.4036	0.4047	0.4058	
17	0.3906	0.3913	0.3929	0.3940	0.3951	0.3962	0.3973	0.3984	0.3995	0.4006	0.4017	0.4023	0.4039	
18	0.3888	0.3899	0.3910	0.3921	0.3932	0.3943	0.3954	0.3965	0.3976	0.3987	0.3998	0.4009	0.4020	
19	0.3869	0.3880	0.3891	0.3902	0.3913	0.3924	0.3935	0.3946	0.3957	0.3968	0.3979	0.3990	0.4001	
20	0.3850	0.3861	0.3872	0.3883	0.3894	0.3905	0.3916	0.3927	0.3938	0.3949	0.3960	0.3971	0.3982	
21	0.3831	0.3842	0.3853	0.3864	0.3875	0.3886	0.3897	0.3908	0.3919	0.3929	0.3940	0.3951	0.3962	
22	0.3812	0.3823	0.3834	0.3844	0.3855	0.3866	0.3877	0.3888	0.3899	0.3910	0.3921	0.3932	0.3942	
23	0.3792	0.3803	0.3814	0.3825	0.3836	0.3847	0.3857	0.3868	0.3879	0.3890	0.3901	0.3912	0.3922	
24	0.3772	0.3783	0.3794	0.3805	0.3816	0.3826	0.3837	0.3848	0.3859	0.3870	0.3881	0.3891	0.3902	
25	0.3752	0.3763	0.3774	0.3785	0.3796	0.3806	0.3817	0.3828	0.3839	0.3850	0.3860	0.3871	0.3882	

Table of the Weight of Substance to be Weighed out—Continued.

Temp. °C.	MILLIMETRES.											
	746	748	750	753	754	756	758	760	762	764	766	768
10°	0.4180	0.4192	0.4203	0.4214	0.4226	0.4237	0.4248	0.4260	0.4271	0.4282	0.4294	0.4305
11	0.4162	0.4173	0.4185	0.4196	0.4207	0.4219	0.4230	0.4241	0.4253	0.4264	0.4275	0.4286
12	0.4144	0.4155	0.4166	0.4177	0.4189	0.4200	0.4211	0.4222	0.4234	0.4245	0.4256	0.4267
13	0.4125	0.4137	0.4148	0.4159	0.4170	0.4182	0.4193	0.4204	0.4215	0.4227	0.4238	0.4249
14	0.4107	0.4118	0.4130	0.4141	0.4152	0.4163	0.4175	0.4186	0.4197	0.4208	0.4220	0.4231
15	0.4088	0.4099	0.4110	0.4122	0.4133	0.4144	0.4155	0.4166	0.4177	0.4188	0.4200	0.4211
16	0.4069	0.4081	0.4092	0.4103	0.4114	0.4125	0.4136	0.4147	0.4158	0.4169	0.4181	0.4192
17	0.4050	0.4061	0.4072	0.4083	0.4095	0.4106	0.4117	0.4128	0.4139	0.4150	0.4161	0.4172
18	0.4031	0.4042	0.4053	0.4064	0.4075	0.4086	0.4097	0.4108	0.4120	0.4131	0.4142	0.4153
19	0.4012	0.4023	0.4034	0.4045	0.4056	0.4067	0.4078	0.4089	0.4100	0.4111	0.4122	0.4133
20	0.3993	0.4004	0.4015	0.4025	0.4036	0.4047	0.4058	0.4069	0.4080	0.4091	0.4102	0.4113
21	0.3973	0.3984	0.3995	0.4006	0.4017	0.4028	0.4039	0.4050	0.4061	0.4072	0.4082	0.4093
22	0.3953	0.3964	0.3975	0.3986	0.3997	0.4008	0.4019	0.4030	0.4041	0.4052	0.4062	0.4073
23	0.3933	0.3944	0.3955	0.3966	0.3977	0.3988	0.3998	0.4009	0.4020	0.4031	0.4042	0.4053
24	0.3913	0.3924	0.3935	0.3945	0.3956	0.3967	0.3978	0.3989	0.3999	0.4010	0.4021	0.4032
25	0.3893	0.3904	0.3914	0.3925	0.3936	0.3947	0.3958	0.3968	0.3979	0.3990	0.4001	0.4012

TABLE XLVIII. (*Text, p. 701.*)

## Specific Gravity of Cement.

Weight of substance taken = 30 g. ; volume of alcohol displaced given in c.c.

c.c.	Sp. Gr.	c.c.	Sp. Gr.	c.c.	Sp. Gr.	c.c.	Sp. Gr.
9.00	3.333	9.30	3.225	9.60	3.125	9.90	3.030
1	3.330	1	3.222	1	3.122	1	3.027
2	3.326	2	3.219	2	3.119	2	3.024
3	3.322	3	3.215	3	3.115	3	3.021
4	3.319	4	3.212	4	3.112	4	3.018
5	3.315	5	3.209	5	3.109	5	3.015
6	3.311	6	3.205	6	3.106	6	3.012
7	3.308	7	3.202	7	3.102	7	3.009
8	3.304	8	3.199	8	3.099	8	3.006
9	3.300	9	3.195	9	3.096	9	3.003
9.10	3.297	9.40	3.191	9.70	3.093	10.00	3.000
1	3.293	1	3.188	1	3.090	1	2.997
2	3.289	2	3.185	2	3.086	2	2.994
3	3.286	3	3.181	3	3.083	3	2.991
4	3.282	4	3.178	4	3.080	4	2.988
5	3.279	5	3.175	5	3.077	5	2.985
6	3.275	6	3.171	6	3.074	6	2.982
7	3.272	7	3.168	7	3.071	7	2.979
8	3.268	8	3.165	8	3.068	8	2.976
9	3.264	9	3.161	9	3.064	9	2.973
9.20	3.261	9.50	3.158	9.80	3.061		
1	3.257	1	3.155	1	3.058		
2	3.254	2	3.151	2	3.055		
3	3.250	3	3.148	3	3.052		
4	3.247	4	3.145	4	3.049		
5	3.243	5	3.141	5	3.046		
6	3.240	6	3.138	6	3.043		
7	3.236	7	3.135	7	3.040		
8	3.233	8	3.132	8	3.036		
9	3.229	9	3.128	9	3.033		

TABLE XLIX. (*Text, p. 741.*)

Table of Hardness, showing the parts per 100,000 of Calcium Carbonate ( $\text{CaCO}_3$ ) for each Tenth of a Cubic Centimetre of Soap Solution when 50 c.c. of the Sample are used.

c.c. of Soap Solution.	0.0 c.c.	0.1 c.c.	0.2 c.c.	0.3 c.c.	0.4 c.c.	0.5 c.c.	0.6 c.c.	0.7 c.c.	0.8 c.c.	0.9 c.c.
0.0	...	...	...	...	...	...	...	0.0	.16	.32
1.0	.48	.63	.79	.95	1.11	1.27	1.43	1.56	1.69	1.82
2.0	1.95	2.08	2.21	2.34	2.47	2.60	2.73	2.86	2.99	3.12
3.0	3.25	3.38	3.51	3.64	3.77	3.80	4.03	4.16	4.29	4.43
4.0	4.57	4.71	4.86	5.00	5.14	5.29	5.43	5.57	5.71	5.86
5.0	6.00	6.14	6.29	6.43	6.57	6.71	6.86	7.00	7.14	7.29
6.0	7.43	7.57	7.71	7.86	8.00	8.14	8.29	8.43	8.57	8.71
7.0	8.86	9.00	9.14	9.29	9.43	9.57	9.71	9.86	10.00	10.15

TABLE L. (*Text, p. 750.*)

Table giving Correction for Titrations with Silver Nitrate Solution by Mohr's Method.

Silver Solution used, in c.c.	Deduction, in c.c.	Silver Solution used, in c.c.	Deduction, in c.c.	Silver Solution used, in c.c.	Deduction, in c.c.	Silver Solution used, in c.c.	Deduction, in c.c.
0.2	-0.20	0.7	-0.38	3.0	-0.46	7.0	-0.54
0.3	-0.25	0.8	-0.39	4.0	-0.48	8.0	-0.56
0.4	-0.30	0.9	-0.40	5.0	-0.50	9.0	-0.58
0.5	-0.33	1.0	-0.41	6.0	-0.52	10.0	-0.60
0.6	-0.36	2.0	-0.44				

TABLE LI. (*Text, p. 787.*)

Table giving the Percentage of Oxygen in Dissolved Air at Various Temperatures.

Temperature.	Oxygen. c.c.	Nitrogen, Argon, etc. c.c.	Total. c.c.	Percentage of Oxygen in the Dis- solved Air.
0	10.19	18.99	29.18	34.91
1	9.91	18.51	28.42	34.87
2	9.64	18.05	27.69	34.82
3	9.39	17.60	26.99	34.78
4	9.14	17.18	26.32	34.74
5	8.91	16.77	25.68	34.70
6	8.68	16.38	25.06	34.65
7	8.47	16.00	24.47	34.60
8	8.26	15.64	23.90	34.56
9	8.06	15.30	23.36	34.52
10	7.87	14.97	22.84	34.47
11	7.69	14.65	22.34	34.43
12	7.52	14.35	21.87	34.38
13	7.35	14.06	21.41	34.34
14	7.19	13.76	20.97	34.30
15	7.04	13.51	20.55	34.25
16	6.89	13.25	20.14	34.21
17	6.75	13.00	19.75	34.17
18	6.61	12.77	19.38	34.12
19	6.48	12.54	19.02	34.08
20	6.36	12.32	18.68	34.03
21	6.23	12.11	18.34	33.99
22	6.11	11.90	18.01	33.95
23	6.00	11.69	17.69	33.90
24	5.89	11.49	17.38	33.86
25	5.78	11.30	17.08	33.82
26	5.67	11.12	16.79	33.77
27	5.56	10.94	16.50	33.73
28	5.46	10.75	16.21	33.68
29	5.36	10.56	15.92	33.64
30	5.26	10.38	15.64	33.60

TABLE LII. (*Text*, p. 876.)

Table for the Determination of Carbon Dioxide in Air  
by Lunge and Zeckendorf's Method.

No of Compressions.	Carbon dioxide content, in parts per thousand.	No of Compressions.	Carbon dioxide content, in parts per thousand.
2	3.00	15	0.74
3	2.50	16	0.71
4	2.10	17	0.69
5	1.80	18	0.66
6	1.55	19	0.64
7	1.35	20	0.62
8	1.15	22	0.58
9	1.00	24	0.54
10	0.90	26	0.51
11	0.87	28	0.49
12	0.83	30	0.48
13	0.80	35	0.42
14	0.77	40	0.38

TABLE LIII. (*Text*, p. 877.)

Maximum Moisture Content in 1 cb.m. of Air, in grams.

*Maximum Vapour Tension of Water in mm. of Mercury  
at different Temperatures of the Air.*

Tempera- ture.	Vapour Tension.	Grams of Water.	Tempera- ture.	Vapour Tension.	Grams of Water.	Tempera- ture.	Vapour Tension.	Grams of Water.
-10°	2.0	2.1	8°	8.0	8.1	21°	18.5	18.2
-8	2.4	2.7	9	8.5	8.8	22	19.7	19.3
-6	2.8	3.2	10	9.1	9.4	23	20.9	20.4
-4	3.3	3.8	11	9.8	10.0	24	22.2	21.5
-2	3.9	4.4	12	10.4	10.6	25	23.6	22.9
0	4.6	4.9	13	11.1	11.3	26	25.0	24.5
1	4.9	5.2	14	11.9	12.0	27	26.5	25.6
2	5.3	5.6	15	12.7	12.8	28	28.1	27.0
3	5.7	6.0	16	13.5	13.6	29	29.8	28.6
4	6.1	6.4	17	14.4	14.5	30	31.6	30.1
5	6.5	6.8	18	15.2	15.1	50	...	83.4
6	7.0	7.3	19	16.3	16.2	70	...	199.3
7	7.5	7.7	20	17.4	17.2			



# INDEX

## SUBJECT INDEX

- ABSORPTION coefficients of gases in water, 225  
 Acids : basicity of, towards different indicators  
     in titrating with sodium hydroxide, 75  
     in chamber gases, determination of, 336  
     in kiln gases, determination of total, 302  
     nitrating and spent, 331  
     standard, 32  
     strength of normal, 93  
     in sulphuric acid making, examination of  
         the, 341  
 "Ados" gas analysis apparatus, 190  
 Air, 866  
     effect of the impurities in, 908  
     estimation of constituents of, 867  
         ammonia, 882  
         aqueous vapour, 877  
         carbon dioxide, 869  
         hydrogen peroxide, 879  
         nitrogen, 869  
         nitrous and nitric acids, 882  
         oxygen, 867  
         ozone, 881  
     estimation of impurities in, 883  
         aniline, 907  
         bromine, 903  
         carbon bisulphide, 905  
         carbon monoxide, 889  
         chlorine, 903  
         cyanogen, 904  
         dust, 901  
         ether vapour, 906  
         hydrocarbons, 896  
         hydrochloric acid, 888  
         hydrocyanic acid, 904  
         hydrofluoric acid, 904  
         hydrogen arsenide, 904  
         hydrogen phosphide, 904  
         hydrogen sulphide, 888  
         iodine, 903  
         mercaptan, 906  
         mercury, 905  
         organic matter, 898  
         phosphorous trichloride, 903  
         soot and smoke, 899  
         sulphur dioxide, 884  
         tobacco smoke, 910  
 Alkali, electrolytic liquors, 442  
     in soda ash, estimation of available, 450  
         977  
 Alkali waste, 435  
 Alkalimetric degrees, English, French, and  
     German commercial, 452  
 Alkalis, standard, 95  
 Alumina, 605  
     analysis of, 619  
 Aluminium salts, 605  
     salts used in dyeing, etc., 620  
     sulphate, analysis of, 608, 610  
         estimation of alumina, 610  
         estimation of free acid, 615  
         estimation of iron, 614  
         estimation of sulphuric acid, 613  
 Alums : potassium, sodium, and ammonium,  
     617  
 Ammonia : determination of, in air, 882  
     determination of, in water, 765  
     -soda process, 439  
         control of working conditions, 440  
         raw materials, 439  
 Ammonium alum, 617  
     chloride or sulphate as standards for  
         acidimetry, 88  
     cyanide, analysis of, 554  
     thiocyanate, 564  
     thiocyanate, standard solutions of, 123  
 Analytical results, calculation of, 183  
 Anemometer : Fletcher's, 170  
     König's differential, 168  
     readings, reducing to current velocity, 171,  
         172  
     readings, temperature corrections for, 172  
 Anemometers, 165  
 Aniline in air, estimation of, 907  
 Areo-pyknometer, 163  
 Arsenic in hydrochloric acid, determination of,  
     415  
     detection and estimation of, in sulphuric  
         acid, 362, 383  
         Bettendorf test, 376  
         Gutzeit test, 374  
         Marsh-Berzelius test, 363  
         Reinsch test, 374  
     in fuel, determination of, 247  
     in pyrites, determination of, 281  
 Arsenious acid : iodometric determination of,  
     122  
     standard solutions of, 122



- Ash in fuel, determination of, 242, 421  
 Atomic weights, international, 185  
 "Autolysator" for determining carbon dioxide in chimney gases, 191  
 Azotometer: Knop's, 125  
                   Wagner's, 131, 132
- BARIUM hydroxide, standard, 99  
 Barothermoscope, the, 148  
 Baryta for glass-making, 629  
 Baumé degrees, converting specific gravity into "rational," 160  
                   hydrometers, comparison of, with specific gravities, 159, 162  
 Bauxite, analysis of, 605  
                   control of working conditions, 607  
                   products from, 608  
 Beet ashes, analysis of, 540  
                   estimation of alkali salts and alkalinity, 541  
                   estimation of moisture, 540  
                   estimation of potassium salts, 541, 542  
                   estimation of sodium carbonate, 542  
 Bitter almond water, analysis of, 549  
 Black ash, examination of, 422  
                   alkali, available, 424  
                   carbonating test, 426  
                   lime, free, 423  
                   lime, total, 424  
                   sodium chloride and sulphide, 425  
                   sodium sulphate, 426  
 Bleaching powder: chlorine, value of, of different strengths, 499, 500  
                   determination of carbon dioxide in, 509  
                   determining strength of, 500  
                   Bunsen's distillation method, 502  
                   Bunsen's iodometric method, 501  
                   Gay Lussac's method, 500  
                   Graham's method, 501  
                   Lunge's method, 504  
                   Penot's method, 503  
                   Pontius' method, 503  
                   Vanino's method, 506  
                   manufacture, 495  
 Bleaching solutions and liquors, analysis of, 509  
                   alkali hydroxide and carbonate, 516  
                   bases, 516  
                   carbonic acid, 514  
                   chlorates, 511  
                   chloride-chlorine, 514  
                   chlorine, available, 509  
                   hypochlorous acid, free, 510  
 Borates: determination of boric acid in, 625  
                   natural, 625  
 Borax, 625  
                   as standard for acidimetry and alkalimetry, 88  
 Boric acid, 624  
                   determination of, 624  
 Brine, 397  
                   analysis of, 398  
 Bromine: determination of, in air, 903  
                   determination of, by iodine, 116  
 Burettes, 46-52  
                   calibrating, 40, 41  
                   gas, 194  
 Burners: Berthelot's, 29  
                   Müncke's, 29  
                   Burners (*cont'd.*): multiple flame, 30  
                                   jet, 30
- CALCIUM, determination of in limestone, 659, 663  
 Calcium sulphide solutions, estimation of sulphide-sulphur in, 438  
 Calspar as standard for alkalimetry and acidimetry, 88  
 Calibration of vessels, 33-46  
 Calorimeter: Berthelot bomb, 254  
                   Fischer's, 250  
                   Parr's, 256  
                   L. Thompson's, 260  
                   W. Thomson's, 262  
 Calorimeters, gas, 226  
                   Boys', 230  
                   Fischer's, 236  
                   Junkers', 226  
 Calorimetry, fuel, 250  
 Carbon: in fuel, determination of, 248  
                   in fuel, determination of fixed, 244  
                   in pyrites, determination of, 288  
 Carbon bisulphide in air, estimation of, 905  
 Carbon dioxide: in air, estimation of, 869  
                   apparatus for determining, 148  
                   in bleaching liquors, estimation of, 514  
                   in chimney gases, apparatus for determining, 190  
                   in the Deacon process, estimation of, 491  
                   in gases, determination of, by Hempel's apparatus, 209  
                   liquid, examination of commercial, 472  
 Carbon monoxide: in air, estimation of, 889  
                   in gases, determination of, by Hempel's apparatus, 210  
 Caustic soda. *See under Soda*  
 Cellulose industry, crude fused soda of the, 443  
 Cement: calcareous, 658  
                   dolomitic or magnesian, 687  
                   hydraulic, 680, 688  
                   Portland, 688, 691  
                   Portland, adulterations of, 727  
                   Portland, analysis of, 692  
                   alkali, total, 694  
                   composition of, 695  
                   ferric oxide, 692  
                   lime, 693  
                   magnesium oxide, 693, 695  
                   sesquioxides, 692  
                   silicates, 692  
                   sodium and potassium, 694  
                   sulphur and sulphuric acid, 693  
 Portland, mechanical tests for, 714  
                   adhesion, 725  
                   bending strain, 726  
                   crushing strain, 724  
                   preparing-test pieces, 715  
                   tensile strain, 721  
 Portland, physical examination of, 698  
                   abrasion test, 717  
                   fineness, 701  
                   frost resistance, 713  
                   hydraulicity, 704  
                   permanency of volume, 706  
                   permeability, 711

- Cement: Portland (*cont.*), specific gravity, 698  
 time of setting, 706  
 Roman, 685
- Chamber acid, 342
- Chamber gases, examination of, 333
- Chance-Claus sulphur recovery process, 437  
 estimation of soda, lime, and thiosulphate, 438  
 estimation of sulphide-sulphur, 437, 438  
 examination of exit gases from Claus kiln, 439  
 examination of gas from gas-holder, 438  
 examination of lime-kiln gases, 438
- Cherry laurel water, analysis of, 548
- Chimney gases: determination of carbon dioxide in, 190  
 loss of heat from, 237
- Chlorates: analysis of, 497  
 estimation of calcium chloride, 498  
 estimation of chlorate, 497  
 estimation of, in bleaching liquors, 511
- Chloric acid, iodometric determination of, 117
- Chlorine: in air, estimation of, 903  
 in bleaching liquors, estimation of available, 509  
 Deacon process, 487  
 determination of carbon dioxide, 491  
 determination of chlorine, 487  
 determination of hydrochloric acid, 490  
 determination of moisture, 495  
 determination of, by iodine, 116  
 industry, the, 476  
 manufacture of, by means of manganese ore, 484  
 properties of liquid, 518, 519  
 weight of 1 c.c. of, 507, 508  
 Weldon process, 485
- Chromic acid, iodometric determination of, 117
- Clay, 568  
 analysis of, 580  
 centesimal analysis, 580  
 rational analysis, 585  
 analysis of, for cement, 688  
 colour, 573, 574  
 density, 575  
 determination of refractoriness, 577  
 physical examination, 569  
 behaviour on drying, 572  
 behaviour on firing, 573  
 mineral mixtures, 569  
 plasticity, 571  
 refractoriness, 576  
 vitrification of, 575
- Claywares, 589  
 chemical analysis, 598  
 determination of composition of fired, 598  
 estimation of alumina in, 600  
 estimation of soluble salts in, 601  
 physical examination of, 589  
 density and porosity, 590  
 durability, 594, 595  
 resistance to fire, 597  
 resistance to wear, 593  
 structure and hardness, 592  
 stability of, towards acids and weathering, 601, 602  
 testing for lead, 599
- Cochineal as an indicator, 77
- Coke, determination of residual, in fuel, 244
- Combustion recorder, the Simmance-Abady, 191
- Congo red: as indicator, 77  
 paper, 80
- Copper in pyrites, determination of, 285
- Copper sulphate, electrolysis of; as basis for acidimetry, 89
- Crucible, Gooch, 25
- Cyanates, determination of, in cyanides, 552
- Cyanides, analysis of, 546, 549, 554, 555  
 Fordos and Gélis' method, 554  
 Liebig's method, 550
- Cyanogen, estimation of, 550, 554  
 compounds, 546
- DEACON chlorine process, 487  
 determination of carbon dioxide, 491  
 determination of chlorine, 487  
 determination of hydrochloric acid, 490  
 determination of moisture, 495
- Dimethylaminoazobenzene as indicator, 67
- Draught, measurement of, 165
- Drips, testing chamber, 341
- Drying precipitates, etc., 27
- EARTHENWARE, 589  
 chemical examination, 598  
 alumina, 600  
 determination of composition, 598  
 lead, 599  
 soluble salts, 600  
 stability towards acids, 601  
 physical examination, 589  
 density, 590  
 durability, 594, 595  
 fire-resisting qualities, 597  
 resistance to wear, 593  
 structure and hardness, 592
- Effluents, 807  
 containing mainly mineral matter, 807  
 containing mainly nitrogenous organic matter, 808  
 contamination due to, 835  
 fish culture, 835  
 industries, 838  
 live stock, 837  
 plants, 839  
 soil, 839  
 waters, 840
- examination of, 811  
 acids, 816  
 albuminoid matter, 826  
 alkalinity, 816  
 carbon, organic, 829  
 carbon dioxide, 832  
 chlorine, 825  
 coal gas products, 833  
 colloidal matter, 814  
 dissolved gases, 813  
 excreta, 832  
 hydrogen sulphide, 825  
 nitrogen, 817  
 oxidisable matter, 815  
 oxygen, 827  
 preliminary tests, 811  
 putrescibility, 833

- Effluents (*contd.*): examination of:
  - residue on evaporation, 812
  - sulphides, 813
  - suspended matter, 825
  - microscopic and bacteriological examination of, 834
  - sampling, 809
- Enamels and enamel colours, 656
- Ether vapour in estimation of, 906
- Evaporation, 22
- FERRIC salicylate as indicator, 77
- Ferrous ammonium sulphate for fixing strength of permanganate solutions, 108
- Filtration, 23, 25
- Flasks, calibrating, 39, 41
- Flint for glass-making, 623
- Fluorometer, 703
- Fluor-spar for glass-making, 629
- Fluxes for glass-making, 627
- Fuel: analysis, 241
  - calorific value of gaseous, 216
  - calorimetry, 250
  - determination of arsenic, phosphorus, and nitrogen in, 247
  - determination of carbon and hydrogen in, 248
  - determination of fixed carbon in, 244
  - determination of moisture and ash in, 242
  - determination of sulphur in, 245
  - sampling, for analysis, 241
- Fusion, 22
- GAS: analysis apparatus, Bone and Wheeler's, 219
  - Fischer's, 198, 215
  - Hempel's, 205
  - Lunge's, 201
  - Orsat's, 198, 201, 203
  - Sodeau's, 203, 219
  - analysis, apparatus for, 194
  - analysis, technical, 189
  - burette: Bunte's, 195
  - Honigmann's, 197
  - Winkler's, 194, 206
  - calorimeter: Boys', 230
  - Fischer's, 236
  - Junkers', 226
  - Junkers', corrections for, 231
  - residuals, sulphur from, 270
  - sampler: Sodeau's, 193
  - Stead's, 193
  - -volumeter, 138
  - table for converting volumes obtained in, into weights of constituents, 246
  - universal, 154
  - -volumetric analysis, 125
- Gases: absorption coefficients of, in water, 225
- calibration of measuring instruments for, 44
- collecting samples of, 191
- determination of carbon dioxide in, 190, 209
- determination of carbon monoxide in, 210
- determination of hydrogen in, 211, 212
- determination of methane in, 213, 214
- determination of oxygen in, 209
- determination of total sulphur in heating, 222
- Oases (*contd.*): in hydrochloric acid manufacture,
  - examination of, 409, 411
  - loss of heat from chimney, 237
  - measuring vessels for, 1, 3
  - storing samples of, 191
  - in sulphuric acid manufacture, examination of, 333
- Gay-Lussac acid, examination of, 342
- Glass, 621
  - action of acids, water, etc., on, 635
  - analysis of, 641
    - qualitative examination, 641
    - quantitative examination, 644
  - analysis of coloured, 655
  - boric acid and borates for, 624
  - colouring agents for, 631
  - decolorising agents for, 630
  - composition of, 634
  - decomposition of for analysis, 644
  - lead glass, 650
  - leadless glass, 644
  - determination of boric acid in, 652
  - determination of fluorine in, 653
  - determination of lead in, 650
  - determination of phosphoric acid in, 654
  - enamels, 657
  - fluxes for, 627, 629
  - lead oxide for, 628
  - lime for, 628
  - production of opacity in, 633
  - silica and silicates for, 620, 623
  - testing, for resistance to weather, water, etc., 635
  - for volumetric analysis, quality of, 54
- Glazes, 589
  - chemical examination, 598
  - alumina, 600
  - determination of composition, 598
  - lead, 599
  - soluble salts, 600
  - stability towards acids, 601, 602
  - physical examination, 589
  - density and porosity, 590
  - durability, 594, 595
  - fire-resisting qualities, 597
  - resistance to wear, 593
  - structure and hardness, 592
- Glover acid, examination of, 342
- Grinding substances, 17
- Gypsum, 729
- HEAT, loss of, from chimney gases, 227
- Heating apparatus, 29
- Humus, determination of, in soils, 857
- Hydrochloric acid: in air, estimation of, 888
  - analysis of, 413
  - arsenic, 415
  - chlorine, 417
  - hydrochloric acid, 417
  - iron, 416
  - residue, 413
  - selenium, 417
  - sulphur dioxide, 416, 417
  - sulphuric acid, 413
  - examination of gases in the manufacture of, 409, 411
  - exit gases, Hargreaves' process, 409

- Hydrochloric acid (*contd.*): in sulphuric acid,  
 • determination of, 383  
 in the Deacon process, estimation of, 490  
 manufacture, 397, 409  
 properties of, 411  
 specific gravity of, 412  
 standard, 82
- Hydrocyanic acid: in air, estimation of, 904  
 analysis of, 548
- Hydrofluoric acid in air, estimation of, 904
- Hydrogen: determination of, by absorption  
 with palladium, 212  
 determination of, by Hempel's apparatus,  
 211  
 in fuel, determination of, 248
- Hydrogen arsenide in air, estimation of, 904
- Hydrogen peroxide: in air, estimation of, 879  
 for permanganate standardisation, 109
- Hydrogen phosphide in air, estimation of, 904
- Hydrogen sulphide: in air, estimation of,  
 888  
 determination of, by iodine, 116
- Hydrometers, comparison of Baumé, with  
 specific gravities, 159, 162
- Hypochlorous acid in bleaching liquors, deter-  
 mination of, 510
- IGNITING precipitates, etc., 27
- Indicators, 55  
 cochineal, 77  
 Congo red, 77  
 diaminoazotoluenesulphonic acid, 76  
 dimethylaminoazobenzene, 67  
 ferric salicylate, 77  
 iodo-eosine, 76  
 lacmoid, 75  
 litmus, 67  
 methyl orange, 61  
 o- and p-nitrophenol, 77  
 phenolphthalein, 71  
 Poirrier's blue C4B, 78  
 rubrescin, 76  
 turmeric, 78  
 basicity of acids towards, 75  
 theory of, 58
- Iodic acid as acidimetric standard, 89
- Iodimetry, 112
- Iodine: in air, estimation of, 903  
 preparation of pure, 120  
 solution, determination of arsenious acid by,  
 122  
 solution, determination of thiosulphates by,  
 117  
 solutions, standard, 113
- Iodo-eosine (indicator), 76
- Iodometric methods for standardising acids and  
 alkalis, 89, 117
- Iron: for permanganate standardisation, 105  
 pyrites. *See* Pyrites  
 in sulphuric acid, determination of, 380
- KILN gases: determination of sulphur dioxide  
 in, 300  
 determination of total acids in, 302
- LACMOID: as indicator, 75  
 paper, 80
- Lead: in sulphuric acid, determination of, 380  
 oxide for glass-making, 628
- Lime: analysis of, 658  
 analysis of quick-, 483  
 analysis of slaked, 484  
 content of milk of lime, 484  
 examination of, 671  
 for glass-making, 628  
 hydraulic, 681  
 analysis of, 681  
 in mortar, determination of, 672  
 valuation of quick-, 669
- Limestone: analysis of, 481, 659, 665  
 determination of calcium oxide or carbonate,  
 482, 659, 663, 667  
 determination of clay, 664  
 determination of insoluble matter, 482  
 determination of iron, 483  
 determination of magnesium oxide, 482,  
 663, 668
- Litmus: as indicator, 67  
 paper, 79
- MAGNESIUM in potash salts, determination of,  
 531
- Manganese and manganese dioxide in Weldon  
 mud, estimation of, 485, 486
- Manganese ore, analysis of, 476  
 determination of carbon dioxide, 481  
 determination of hydrochloric acid necessary  
 for decomposition, 481  
 determination of moisture, 477  
 determination of active oxygen, 477
- Manometers: differential, 167  
 Langen's, 169
- Marls, examination of, 683
- Measuring: liquids, 39  
 vessels for gases, 155
- Mercaptan in air, estimation of, 906
- Mercuric cyanide, analysis of, 555
- Mercury vapour in air, estimation of, 905
- Methane: combustion of, by heated platinum  
 wire, 214  
 in gases, determination of, 213
- Methyl orange: as indicator, 61  
 paper, 80
- Moisture: in coal, etc., determination of, 242,  
 420  
 in Deacon gases, determination of, 495  
 in manganese ore, determination of, 477
- Mortar, determination of lime in, 672
- NESSLER'S reagent, 766
- Nitrate in saltpetre, determination of, 309  
 ignition method, 318  
 Lunge's nitrometer method, 315  
 "Nitron" method, 311  
 Schlösing-Grandeau-Wagner method, 317  
 Ulsch-Bückmann method, 311
- Nitrating acids, examination of, 331
- Nitre. *See* Potassium nitrate
- Nitric acid, 323  
 manufacture, 306  
 specific gravity, 324  
 standard, 83  
 in sulphuric acid, determination of, 379  
 and sulphuric acid, mixtures of, 331

- Nitric acid (*contd.*): testing, 328
  - acidity, total, 329
  - chlorine, 330
  - iodine, 330
  - metals, 330
  - nitrogen peroxide, 328
  - residue, fixed, 329
  - sulphuric acid, 330
- Nitric oxide in chamber gases, determination of, 338
- Nitrogen: absorption, Dietrich's table for, 128
- in air, estimation of, 869
- Dietrich's table for weight of 1 c.c. of, 129, 130
- in fuel, determination of, 247
- in soils, determination of, 861, 862
- Nitrogen peroxide, estimation of, 328
- Nitrometer, the, 132
- Nitrosity of drips, determination of, 341
- Nitrous acid in nitrous vitriol, determination of, 343
- Nitrous oxide in chamber gases, determination of, 340
- $\alpha$ - and  $p$ -nitrophenol as indicators, 77
- OLEUM. *See* Sulphuric acid, fuming
- Oxalic acid: as basis for alkalimetry and acidimetry, 82, 83, 91
- normal, 94
- standardising permanganate by, 103
- Oxide, spent, examination of, 555
- moisture, 556
- Prussian blue, 556
- manufacture of ferrocyanide from, 561
- manufacture of thiocyanates from, 564
- Oxygen: in air, estimation of, 867
- in chamber gases, determination of, 334
- in gas mixtures, determination of, by Hempel's apparatus, 209
- in manganese ore, determination of active, 477
- Ozone, in air, estimation of, 881
- PERCHLORIC acid, preparation of, 523
- Permanganate. *See* Potassium permanganate
- Peroxides, iodometric determination of, 117
- Phenolphthalein: as indicator, 71
- paper, 80
- Phosphorus trichloride in air, estimation of, 903
- Phosphorus in fuel, determination of, 247
- Pipette, Hempel's explosion, 213
- Ostwald's, 42
- Pipettes, 53
  - calibrating, 39, 40, 41
- Poirrier's blue C4B as indicator, 78
- Potassium, determination of, 527, 528
- perchloric acid method, 522, 530
- platinichloride method, 520, 528
- other methods, 524
- Potassium alum, 617
- bichromate in alkalimetry, 93
- bi-iodate as acidimetric standard, 89
- carbonate, analysis of, 543, 545
- carbonate, determination of sodium carbonate in, 544
- carbonate for glass manufacture, 627
- Potassium carbonate manufacture, 540
  - by-products, 543
  - final products, 543
  - intermediate products, 543
  - raw materials, 540
  - chlorate, analysis of, 497, 498, 517
  - chlorate manufacture, 497
  - chloride, analysis of, 533, 540
    - determination of insoluble matter and moisture, 535
  - determination of magnesium salts, 535
  - determination of potassium, 533
  - determination of sodium chloride, 534
  - cyanide, analysis of, 549
  - ferrocyanide, 563
  - ferrocyanide, 555, 562
  - manufacture of, from spent oxide, 561
  - hydrogen tartrate as standard for acidimetry, 93
  - hydroxide, standard, 99
  - nitrate, analysis of, 538, 539
  - nitrate, estimation of, in chlorate, 517
  - permanganate, standard, 99
  - standardising, by ferrous ammonium sulphate, 108
  - standardising, by hydrogen peroxide, 109
  - standardising, by iron method, 105
  - standardising, by nitrometer method, 109
  - standardising, by oxalic acid, 103
  - standardising, by Volhard's iodometric method, 109
- salt manures, analysis of, 537
- salts, analysis of, 520, 528, 531, 533
  - determination of magnesium, 531
  - determination of potassium, 520, 528
  - determination of sulphuric acid, 531
- sulphate, analysis of, 535
- sulphate, determination of potassium in, 536, 537
- thiocyanate, 567
- Precipitates, washing and filtering, 23
- Precipitation, 23
- Pressure-gauges, 165
- Prussian blue, determination of, 556
- Drehschmidt's method, 560
- Knublauch's method, 557
- Moldenhauer and Eybold's method, 560
- Nauss' method, 558
- Zulkowsky's method, 558
- Puzzuolanas: artificial, 679
- natural, 674
- Pyrites: determination of arsenic in, 281
- determination of carbonates and carbon in, 288
- determination of copper in, 272, 285
- determination of lead and zinc in, 287
- determination of moisture in, 272
- determination of sulphur in, 272, 294
- distinguishing ordinary and magnetic, 289
- Pyrometers: air, 175
- calorimetric, 178
- electric resistance, 179
- expansion, 175
- fusion point, 176
- optical, 177
- thermo-electric, 180
- and pyrometry, 174

QUARTZ for glass-making, 623  
Quicklime. *See* Lime

RUBRESCIN (indicator), 76

SALT: analysis of, 400  
chlorine, 401  
insoluble matter, 402  
moisture, 400  
sulphuric acid, 401  
works, 397

Saltcake: analysis of, 404  
aluminium, 407  
calcium, 405  
free acid, 404  
insoluble matter, 405  
iron, 405  
magnesium, 406  
sodium chloride, 404  
sodium sulphate, 408  
manufacture of, 397, 419

Saltpetre, Chili, 306  
assay of, 307  
complete analysis of, 308  
estimation of nitrate in, 309  
estimation of perchlorate in, 319  
Samples: of gases, collecting, 191  
storing, 192  
collection and storage of, 16  
taking, 7-17

Sampling: caustic soda, 465  
effluents, 809  
fuel, 241  
gases, 191  
liquids, 14  
materials in large pieces, 9  
powdered chemicals, 13  
raw materials in powder, dross, etc., 12  
soils, 843

Sand for glass-making, 622  
Santorin earth, 674  
"Sarco" gas analysis apparatus, 190  
Seeger's fusible cones, 176  
Sewage, 807

examination of, 811  
acids, 816  
albuminoid matter, 826  
alkalinity, 816  
carbon, organic, 829  
carbon dioxide, 832  
chlorine, 825  
coal-gas products, 833  
colloidal matter, 814  
dissolved matter, 813  
excreta, 832  
hydrogen sulphide, 825  
nitrogen, 817  
oxidisable matter, 815  
oxygen, 827  
preliminary tests, 811  
putrescibility, 833  
residue on evaporation, 812  
sulphides, 813  
suspended matter, 825

Silica for glass-making, 620  
Silicates for glass-making, 620, 623  
Silver nitrate, standard solutions of, 123

Slack for sodium carbonate manufacture, 420  
Slates, examination of roofing, 602

Soda ash, 447  
analysis (complete) of, 456  
estimation of available alkali in, 450  
examination of, 453  
*See also* Sodium carbonate

Soda, caustic, 463  
analysis of, 466  
electrolytic liquors, 442  
examination of products in manufacture of, 441

caustic bottoms, 441  
causticised liquor, 441  
fished salts, 441  
lime mud, 442  
sampling, 465  
specific gravity of solutions of, 463, 464

Soda crystals, 462  
Soda of the cellulose industry, crude fused, 443  
Sodium: in potassium chloride, estimation of,

534  
as standard for acidimetry and alkalimetry, 88

Sodium alum, 617  
aluminate, 617  
bicarbonate, 467  
analysis of, 468  
estimation of total carbon dioxide in, 469  
carbonate, analysis of crude, 450, 453, 456  
available alkali, 450, 458  
insoluble matter, 457  
physical and qualitative tests, 453, 454, 455, 459

sodium carbonate, 458  
sodium salts other than carbonate, 455, 456, 457  
carbonate, determination of, in carbonated liquors, 429  
in potassium carbonate, 544  
in soda liquors, 429  
in vat liquors, 426  
in vat waste, 436

carbonate for glass manufacture, 627  
carbonate, manufacture of, 419  
calcium carbonate for, 420  
Leblanc process, 419  
black ash, 422  
carbonated liquors, 429  
saltcake, 419  
slack for, 420  
soda mother liquors, 429  
vat liquor, 426  
vat waste, 435

Solvay process, 439  
carbonate, pure, examination of, 460  
carbonate, purification of, for volumetric analysis, 83  
carbonate solutions, specific gravity of, 447  
carbonate as standard for acidimetry and alkalimetry, 83  
*See also* Soda ash

chloride, 399  
analysis of, 400, 403  
chlorine, 401  
insoluble matter, 402  
moisture, 400

- Sodium chloride (*contd.*): determination of sul-  
 • phuric acid in, 401  
 • pure, 403  
 cyanide, analysis of, 554  
 ferrocyanide, 563  
 hydrosulphite as oxygen absorbent in gas  
 analysis, 209  
 hydroxide, normal, 96  
 nitrate. *See* Saltpetre, Chili  
 perchlorate, estimation of, in sodium nitrate,  
 319  
 sulphate for glass manufacture, 627  
 sulphate in saltcake, estimation of, 408  
 sulphide, sulphite, sulphate, and thiosul-  
 phate, simultaneous determination of,  
 430
- Soils, 841  
 chemical examination, 851  
 acids, treatment with various, 852-856  
 determination of carbon dioxide, 859  
 determination of chlorine, 852  
 determination of humus, 857  
 determination of metals, 864  
 determination of nitrogen, 861  
 determination of sulphur, 862  
 determination of water, 857  
 mechanical examination, 844  
 physical examination, 848  
 absorptive power for salts in solution, 849  
 capacity for water, 849  
 capillary attraction, 849  
 evolution of heat on moistening, 851  
 sampling, 843
- Solution, 22  
 Solutions, normal, 80  
 Specific gravities: comparison of Baumé hy-  
 drometers with, 159, 162  
 • converting, into "rational" Baumé degrees,  
 160  
 determination of, 156
- Stassfurt salts, examination of, 528  
 crude salts, analysis of, 528, 531  
 intermediate and finished products, 533
- Sulphides, iodometric determination of, 116
- Sulphite liquors, for wood-pulp making,  
 examination of, 306
- Sulphites, determination of, 305
- Sulphur: analysis of native, 266, 294  
 determination of, 268, 277, 294  
 determination of arsenic and selenium in, 267  
 determination of ash, moisture, and bitumin-  
 ous substances in, 266  
 determination of, in the Chance-Claus pro-  
 cess, 437, 438  
 determination of, in coal, etc., 245, 247  
 • determination of, in pyrites, 272, 294  
 determination of, in soils, 862  
 • determination of total, in heating gases, 239  
 • determination of, in vat liquor, 427  
 determination of, in vat waste, 436  
 • determination of, in zinc blende, 289, 293,  
 298  
 from gas residuals, 270, 294  
 native, 264  
 specific gravities of solutions of, in carbon  
 bisulphide, 269
- Sulphur dioxide: in air, estimation of, 884  
 • in kiln gases, determination of, 290  
 • *See also* Sulphurous acid and Sulphur  
 anhydride  
 Sulphuretted hydrogen. *See* Hydrogen sul-  
 phide  
 Sulphuric acid, 346  
 analysis of, 359  
 detection and estimation of arsenic in, 362  
 383  
 Bettendorf test, 376  
 • Gutzzeit test, 374  
 Marsh-Berzelius test, 363  
 Reinsch test, 374  
 determination of, 277, 377  
 determination of hydrochloric acid, 383  
 determination of iron and lead, 380  
 determination of nitric acid, 379  
 determination of nitrous acid, 343, 377  
 determination of sulphur dioxide, 377  
 examination of, 359, 377  
 fuming, 385  
 analysis of, 387  
 boiling points, 385  
 melting points, 385  
 specific gravity, 386  
 gases in the manufacture of, examination of,  
 333  
 acids, 336  
 nitric oxide, 338  
 nitrous oxide, 340  
 oxygen, 334  
 manufacture, 333  
 melting and boiling points, 358, 385  
 and nitric acid, mixtures of, 331  
 specific gravity of various strengths of, 348  
 standard, 82
- Sulphuric anhydride, determination of, 387
- Sulphurimeter, the, 265
- Sulphurous acid: determination of sulphur  
 dioxide in, 304  
 kiln gases, examination of, 299  
 manufacture, 264, 294  
 solutions, specific gravities of, 305  
*See also* Sulphur dioxide  
 Sulphurous anhydride, liquid, 305  
*See also* Sulphur dioxide
- TEMPERATURE, measurement of, 172  
 • "Tenax" apparatus, for estimation of dissolved  
 gases in water, 827  
 Test papers, 79-80  
 Thalpotsimeter, 175  
 Thermometers and thermometry, 17  
 Thermophone, Wiborg's, 177  
 • Thiocyanates, 564  
 Thiosulphates, iodometric determination of,  
 117
- Titration, vessels for, 54
- Tobacco smoke, 310
- Trass, 674  
 examination of, 676
- Turmeric: as indicator, 78  
 paper, 80
- VAT liquor and waste. *See under* Sodium  
 carbonate

Vessels, calibration of, 33-46

Vicat needle, 706

Volumometer, Schumann's, 698

Volumenometer for mortar, Michaelis, 670

Volumetric analysis, calibrating and standardising apparatus for, 31

WATER: analysis, interpretation of results of, 793

bacteriological examination, 789

counting the bacteria, 791

nutrient gelatin, 790

optical examination, 736

acidity, 738

alkalinity, 737

ammonia, 765

ammonia, albuminoid and proteid, 769

calcium, 764

carbonic acid, 762

chlorine, 750

dissolved gases, 776

hardness, 739

hydrogen sulphide, 786

iodine, 751

iron, 773

lead, 775

magnesium, 764

methane, 777

nitric acid, 751

nitrogen (dissolved), 777

nitrous acid, 759

Water, chemical examination (*contd.*):

oxygen absorption, 742

oxygen (dissolved), 777

phosphoric acid, 762

potassium, 764

residue on evaporation, 736

silica, 748

sodium, 764

sulphuric acid, 748

drinking, 733

for boilers and other technical purposes,

799

tests for, 800

microscopic examination, 789

physical examination: clearness, colour,

smell, and taste, 734

temperature, 734

Weighing, 19

Weldon: mud, examination of, 485

estimation of "base," 486

estimation of manganese, 486

estimation of manganese dioxide, 485

process, the, 485

ZINC blende: determination of fluorine and

available sulphur, 293

determination of lead, calcium, magnesium,

arsenic, and carbonic acid, 292

determination of sulphur and zinc, 289,

298

Zinc oxide for glass-making, 629



## NAME INDEX

- ADAM, E.—glass, analysis of, 646  
 glass, detection of boric acid in, 642  
 glass, lead, 650  
 Adeney—water, apparatus for extracting and analysing gases in, 780  
 water, dissolved gases in, 785, 786  
 Ahrens and Gilbert—perchlorates in presence of iodate, determination of, 321  
 Alberti and Hempel—saltpetre, examination of, 319  
 Allen—hydrochloric acid, purifying, for the Marsh test, 373  
 Amsler and Laffon—cement, apparatus for examining the permeability of, 713  
 Andrews—sulphuric acid, determination of, 278  
 Angerstein—sampling auger, 14  
 Appert and Henrivaux—glass, estimation of alkali in, 649  
 Arens. *See* Lehmann, 901  
 Arnould—chloride, chlorate, and perchlorate, estimation of, in mixtures, 322  
 Atterberg—arsenic in sulphuric acid, determination of, 384  
 Autenrieth and Windaus—sulphate and thio-sulphate, separation of, 432  
 Avery and Dales—iron, purity of electrolytic, 107  
 Aykroyd. *See* Richardson, 434
- BACHOFEN. *See* Lunge, 499  
 Bailey, G. H.—air, determination of sulphurous acid in, 885  
 Balthaser. *See* Prost, 293  
 Barbieri and Neppi—ferrous oxalate for standardising permanganate, 105  
 Barthel—petroleum burner, 31  
 Baud—bauxite, analysis of, 606  
 Baumann, A.—gas analysis with the azotometer, 126  
 manganese ore, estimation of active oxygen in, 480  
 standardisation of acids, 89  
 Baur and Cramer—calcium carbonate in limestone, apparatus for determining, 660  
 Bauschinger—cement, apparatus for applying the abrasion test to, 714  
 expansion of cement, apparatus for testing, 707  
 Bayer—potassium, determination of, 524  
 Beck, H.—oxalic acid solutions, sterilised, 95  
 Beckurts—iodates in saltpetre, determination of, 307  
 iodine in nitric acid, test for, 331
- Beilstein and Grosset—aluminium sulphate, estimation of free acid in, 616  
 Berdel—clays, analysis of, 586  
 Berg—iodine and sulphurous acid, reaction between, 116  
 Bergmann—burettes, device for reading, 47  
 Berthelot—calorimeter, bomb, 254  
 Bertrand—arsenic, determination of, 371  
 Bettendorf—arsenic test for, 376  
 Beutell—float for burettes, 48  
 Bevan. *See* Cross, 66, 618  
 Biltz—ferrous sodium sulphate for standardising permanganate, 108  
 Bischof, C.—clays, determining refractoriness of, 577  
 Blacher—water for boilers, etc., examination of, 805  
 Black, O. F. *See* Sanger, C. R., 376  
 Blake. *See* Letts, 872  
 Blakey. *See* North, 85, 90  
 Blattner—eau de Javel, analysis of, 516  
 lime content of milk of lime, 484  
 and Brasseur—arsenic in pyrites, estimation of, 282, 283  
 perchlorate in Chili saltpetre, determination of, 320, 322  
 Bleier, O.—measuring vessels, 53  
 Blount. *See* Stanger, 693  
 Blum, L.—aluminium sulphate, analysis of, 610  
 Bückmann—arsenic in sulphuric acid, determination of, 384  
 litmus as indicator, 68  
 nitrate in saltpetre, determination of, 311  
 salt, determination of moisture in, 401  
 sulphur in iron pyrites, determination of, 295  
 Böhme—cement briquettes, hammer for moulding, 718  
 Bone, W. A., and R. V. Wheeler—gas analysis apparatus, 219  
 Bornträger—potassium hydrogen tartrate as standard for acidimetry, 93  
 Bousfield and Lowry—sodium hydroxide solutions, preparation of standard, from sodium, 96  
 sodium hydroxide solutions, specific gravity of, 463, 464  
 Boys—gas calorimeter, 230  
 Brasseur. *See* Blattner, 282, 283, 320, 322  
 Bredig and Winkelblech—indicators, theory of, 59  
 Brisee. *See* Kohn, 108  
 Brown, H. T., and Escombe—carbon dioxide in air, estimation of, 873

- Brown, J. C.—sewage, etc., determination of nitrogen in, 818  
 Browning and Howe—sulphur compounds, estimation of, in soda mother liquors, 433  
 Brulins—iodine solutions, standardising, by bichromate, 115  
 Brunck, O.—hydrogen and methane, combustion of, 211  
 Brünner—slates, examination of roofing, 603  
 Buchanan—borax as basis in acidimetry, 88  
 Bullheimer—fluorine in zinc blende, determination of, 293  
 Bunsen—absorption coefficients of gases in water, 225  
 Bleaching powder, analysis of, 501, 502  
 Iodometric methods of volumetric analysis, 112  
 Bunte—gas burette, 195  
 Burgess, T. W.—tintometer for water, 735  
 Busch—nitrate in saltpetre, determination of, 311  
 CALDWELL. *See* Macfarlane, 219  
 Callendar, W. L.—pyrometer, electric resistance, 179  
 Carpenter, T. B.—sulphur, determination of moisture in, 266  
 Caspari—perchloric acid, preparation of, 523  
 Chambers. *See* Morse, 89, 109  
 Chancel—sulphurimeter, 265  
 Chapman and Law—arsenic, determination of, 371  
 Chlopin—oxygen in air, determination of, 867  
 Chorley. *See* Plimpton, 122  
 Christie. *See* Treadwell, 493, 494  
 Clar and Gaier—sulphuric anhydride or fuming sulphuric acid, analysis of, 388  
 Clark—arsenic in pyrites, determination of, 284  
 sulphur in pyrites, determination of, 277  
 water, determination of hardness of, 740  
 Clarkson—"rapid sampler," 10  
 Classen—iron, electrolytic, for standardising permanganate, 107  
 Clennel—cyanogen, estimation of, 551  
 Cobb, J. W.—glazed bricks, testing, 596, 602  
 Cohen, J. B. *See* Oddy, 101  
 Cohn, A. I.—indicators and test-papers, 55  
 Cone—pyrites, distinction between ordinary and magnetic, 289  
 Conroy—ferrocyanides, estimation of, 562  
 sodium ferrocyanide, manufacture of, 563  
 Contat—iron wire, apparatus for dissolving, in acid, 106  
 Cramer, E. *See* Seger, H., 802  
 Crato, E.—potassium bi-iodate for standardising normal sodium carbonate solution, 93  
 Crismer—thiosulphate, potassium chromate for standardising, 121  
 Croasdale. *See* Hart, 89  
 Cross and Bevan—alumina, titration of, 66, 618  
 Cushman—pipette, improved form of Ostwald, 43  
 DALES. *See* Avery, 107  
 Dauvé—copper sulphate, electrolysis of, as basis for acidimetry, 89  
 Davidson. *See* Kolb, 513  
 Débourdeaux—manganese ore, analysis of, 481  
 De Haën—ferrocyanides, estimation of, 561  
 sodium ferrocyanide in "vat liquor," estimation of, 427  
 De Koninck—iodine, preparation of pure, 119  
 permanganate solutions, action of, on rubber, 102  
 starch solution, 114  
 Denham, H. G.—hydrogen and methane, combustion of, 211  
 Denigés—bleaching powder analysis, 500  
 Desbordes. *See* Gauntlett, 175  
 Deville—furnace, universal, 32  
 Diamant—potassium, determination of, 526  
 Dietrich—nitrogen absorption tables, 128-130  
 nitrogen, table for weight of 1 c.c. of, 129  
 Dietz and Margosches—thiosulphate, standardising, by potassium chlorate, 121  
 Dié—bleaching liquors, analysis of, 512  
 Divers—nitric acid, absorption of, in gas analysis, 339  
 Dobriner and Schranz—sulphuric acid, fuming, analysis of, 393  
 Donath—arsenic, test for, 376  
 Drehschmidt—carbon monoxide, absorption of, by cuprous chloride, 210  
 methane, combustion of, by a hot platinum wire, 214  
 Prussian blue, analysis of, 560  
 Dupré—burettes, reading, 50  
 cochineal as indicator, 78  
 perchlorates, determination of, 321  
 titrating, vessels for, 54  
 Volhard's method of permanganate determination, 109  
 and Kupffer—potassium tetroxalate in acidimetry, 92  
 EBELING—iron in sulphuric acid, determination of, 381  
 Eichhorn—areo-pyknometer, 163  
 Engel and Ville—Poirrier's blue as indicator, 78  
 Engler and Wild—ozone in air, test for, 881  
 Erck—perchlorate in Chili saltpetre, determination of, 320  
 Erdmann—float for burettes, 47  
 nitrous acid in sulphuric acid, estimation of, 361  
 Erdmenger and Mann—cement, apparatus for finding specific gravity of, 699  
 Eschka—sulphur in coal, determination of, 245, 246, 421  
 Escombe. *See* Brown, H. T., 873  
 FABRE—potassium, determination of, 526  
 Fahlberg and Iles—sulphur in pyrites, determination of, 277  
 Feichtinger—santorin earth, 675  
 Feld—sulphur, determination of, 432  
 Feldhaus—cyanogen in cherry laurel and bitter almond waters, estimation of, 548  
 Fellner—hydrofluoric acid in air, estimation of, 904  
 Fenton—saltcake, determination of total sodium in, 408

- Fery—pyrometer, radiation, 178
- Fessell—acidimetry, iodometric method of, 89
- Filsinger and Elsner—soap solutions, analysis of, 67
- Finkener—iodine and sulphurous acid, reaction between, 115
- Fischer, F.—calorimeter, 250
  - chimney gases, loss of heat from, 238
  - coal, determination of carbon and hydrogen in, 248, 249
  - coal, determination of nitrogen in, 247
  - gas analysis apparatus, 198, 215
  - gas calorimeter, 236
  - gases from a Bessemer converter, sampling, 192
- Fischer and Philipp—dimethylaminoazobenzene as indicator, 67
- Fleischer, M.—soils, determination of sulphur in, 863
- Fleming-Stark—Orsat apparatus for chlorine, simplified, 495
- Fletcher—anemometer, 170
- Fodor—carbon monoxide in air, estimation of, 890
- Förster, F.—glass, action of water, acids, etc., on, 636
  - lacmoid as indicator, 75
  - litmus solution, 68
  - and Mylius—glass, determination of action of water on, 641
- See Mylius, 76
- Förster, O.—perchlorate in Chili saltpetre, determination of, 320
- starch, preparation of soluble, 114
- Forchhammer—clays, rational analysis of, 585
- Fordos and Gélis—cyanides, analysis of, 547, 554
- Fowler—sewage, etc., determination of nitrogen in, 817
- and Arden—sewage, determination of colloidal matter in, 814
- Frankland and Ward—gas analysis apparatus, 215
- Franzen, H.—sodium hydrosulphite, as absorbent for oxygen, 209
- Frerichs, G.—lead in water, estimation of, 775
- Fresenius, H.—arsenic in pyrites, estimation of, 285
- Fresenius, W.—analytical results, calculation of, 186
  - calcspar as basis for acidimetry, 88
  - chlorates in bleaching solutions, determination of, 511
  - sulphur in pyrites, determination of, 275
- Friendenthal—indicators, sensitiveness of, 78
- Fritsch and Venator—aluminium plates as substitute for sand-baths, 23
- Fritzsche, P.—soot in factory chimneys, determination of, 900
- Froysell. See Kohn, 108
- Frühling—lime in mortar, determination of, 672
- Fuchs, P.—temperature corrections for hydrometers, 164
- GAIER. See LIAR, 300
- Gans, R.—soils, determining absorption of salts by, 851
- Gardner and others—potassium permanganate, purity of, 103
- Gastine—carbon bisulphide in air, estimation of, 905
- Gauntlett and Desbordes—pyrometer, expansion, 175
- Gautier—carbon monoxide in air, estimation of, 895
- Gawalowski—burettes, filling, 51
  - sampling auger, 13
  - sampling pipette, 15
- Gélis. See Fordos, 547, 554
- Genzken. See Strache, 191
- Gerlach—Baumé degree, value of, 157
- Gilbert, C.—perchlorates, determination of, 321
- Gilbert, H. See Ahrens, 321
- Gilbert—potassium, determination of, 527
- Giles and Shearer—sulphurous acid solutions, specific gravities of, 305
- Gintl—iron in sulphuric acid, determination of, 381
  - palladium wire saturated with hydrogen as a reducing agent, 109
- Glaser, F.—indicators, 55
  - methyl orange, sensitiveness of, 62
  - p-nitrophenol as indicator, 77
  - test-papers, sensitiveness of various, 79
- Glücksman—iodo-eosine as indicator, 76
- Gückel—burettes, reading, 44, 49
  - burette for titrating hot solutions, 52
  - hydrometers, marking of, 164
  - iron wire, apparatus for dissolving, 106
  - pipettes, 41
  - standardising apparatus, 33
- Goldberg and Naumann—p-nitrophenol as indicator, 77
- Graeger—ferrous sodium sulphate for standardising permanganate, 108
- Graham—bleaching powder, analysis of, 501
- Grandeau—calcspar as basis for acidimetry, 88
- Griess—nitrous acid in water, detection of, 760
- Griffin and Goreham—flowmeter, 703
- Gröger—acidimetry, iodometric method of, 89
  - alkali, iodometric estimation of free, 117
- Groll. See Verwer, 108
- Grosset. See Beilstein, 616
- Grossmann—sulphide, sulphate, sulphite, and thiosulphate, simultaneous estimation of, 430
  - sulphuric acid, determination of, 279
- Grünhut—sulphuric acid, fuming, table for finding the free  $\text{SO}_2$  in, 395
- Grütters. See Kjister, 57, 97
- Grützner—nitrous acid, determination of, 343
- Grundmann, R.—soils, determination of copper and lead in, 864
- Gruner—carbon in fuel, determination of fixed, 344
- Gruszkiewicz—gas volumeter, 145
- Guttmann—spent acid, composition of, 332
- Gutzeit—arsenic, test for, 374

- Gyzander—aluminium sulphate, determination of sulphuric acid in, 613
- HÄBER, F.—chancey gases, estimating the composition of, 191
- Hackford. *See* Sand, 371
- Häfcke. *See* Vogel, 525
- Hager—arsenic in hydrochloric acid, test for, 414
- sulphur, determination of arsenic in, 267
- Haldane, J. S.—air, calorimetric test for carbon monoxide in, 892
- air, determination of sulphur dioxide in, 886
- carbon dioxide in air, estimation of, 873
- Hampe—oxalic acid, anhydrous, in acidimetry, 91
- Harbeck and Lunge—benzene in air, determination of, 898
- Hart and Crossdale—copper sulphate, electrolysis of, as basis for acidimetry, 89
- Hartley—sodium as basis for acidimetry, 88
- Hase—analytical balance, 20
- Haselhoff—water, harmful quantities of substances, 836
- Hasenclever—carbon dioxide in Deacon gases, estimation of, 491
- Hasseidter, V.—zinc in blende, estimation of, 289
- Hattensaur—arsenic in sulphuric acid, determination of, 384
- Hauenschild—cement, detection of adulteration of Portland, 717
- Hawliczek—cyanogen in "vat liquor," estimation of, 428
- Hehner—arsenic, determination of, 372, 375
- sulphuric acid, arsenic in, 363
- water, determination of alkalinity of, 800
- Heim, L.—air, determination of soot and smoke in, 900
- Heinrich—carbon in fuel, determination of fixed, 244
- Heintzel—cement, calcining test for, 709
- Hempel—calorific value of gas, apparatus for determining the, 237
- fluorine in fluor spar, estimation of, 630
- gas analysis, apparatus for, 205
- hydrogen, absorption of, by palladium, 212
- permanganate solutions, standardising, by oxalic acid, 103
- pipette, explosion, 213
- pyrometer, optical, 177
- See* Albert, 319
- Hendrixon—chlorates, determination of, 513
- Henriques—thiocyanates and silver nitrate, reaction of, 124
- Henrvaux. *See* Appert, 649
- Heraeus—Seger cones, fusion temperatures of, 177
- Herspath—iron in aluminium sulphate, determination of, 614
- Herting—cyanates, determination of, 552
- Hertz—zinc in blende, estimation of, 291
- Hersfeld—cement, determination of alkalis in, 602
- Higgins—hydrochloric acid solutions, preparation of standard, 90
- sodium carbonate as basis for acidimetry, 85
- Hilgard—potassium, determination of, 526
- Hilger—hydrochloric acid, test for sulphurous and arsenious acids in, 417
- Hille. *See* Troeger, 76
- Hillebrand—cement analysis, 692
- glass, analysis of, 646
- Him'y, C.—effluents, detection of coal gas products in, 833
- Hinmann—potassium tetroxalate in acidimetry, 92
- Hintz—sampling, 9
- Hirsch—titration with phenolphthalein in alkaline solution, 74
- Hock. *See* Traub, 75
- Hönig—perchlorate in Chili saltpetre, determination of, 320
- and Spitz—boric acid in silicates, estimation of, 652
- Holmblad—lime in mortar, determination of, 673
- Hosigmann—gas burette, 197
- Horsley, J.—effluents, etc., determination of nitrates in, 821
- Howe. *See* Browning, 433
- Huber, H. v.—bleaching liquors containing chromate, examination of, 517
- Hundeshagen—sulphur in coal, determination of, 422
- Hunter. *See* Lunge, 8
- ILZS. *See* Fahlberg, 277
- Ilosvay, L.—acetylene in air, detection of, 897
- nitrous acid in sulphuric acid, detection of, 360
- Immendorff—soils, determination of carbon dioxide in, 859
- Isbert and Venator—sodium sulphate in salt cake, determination of, 408
- Isler—sulphuric acid solutions, specific gravity of, 347, 350
- JAHODA—ferrous sulphate solution, preparation of, 106
- See* Strache, 191
- Jannasch—glass, analysis of, containing boric acid, 653
- Japp—gas-volumeter, the, 147
- Jørgensen—boric acid in borates, estimation of, 625
- John. *See* Perman, 88
- Jones, C.—boric acid, examination of, 624
- Junker—gas calorimeter, 226
- Juon—metallurgical sampling, 9
- KALMANN—iodine solutions, standardisation of, 115
- and Spüller—sulphate, sulphite, sulphide, and thiosulphate, simultaneous estimation of, 431
- Kammerer—claywares, determining stability of, towards acids, 602
- Kéler. *See* Lunge, 608
- Kessler—permanganate and hydrochloric acid, interaction of, 102

- Kiepen, P.—alumina, analysis of, 619, 620  
 bauxite, analysis of, 603  
 Kirkby—Gutzzeit test for arsenic, modified, 373  
 Kissling, R.—glass, examination of, 640  
 Kjeldahl—acidimetry, iodometric method of, 89  
 and Jodlbaur—sewage, etc., determination of  
 nitrogen in, 817  
 Klinghammer—thalpotastimeter, 175  
 Knietsch, R.—chlorine, pressure and specific  
 gravity of liquid, 519  
 sulphuric acid, fuming, boiling and melting  
 points of, 385  
 specific gravity of, 386  
 table for finding per cent. of free  $\text{SO}_2$   
 in, 394  
 sulphuric acid, melting points of, 358  
 Knöfser—burette and stock-bottle combined, 52  
 Knop—azotometer, 125  
 soils, determination of absorptive power of,  
 for salts, 850, 859  
 Knublauch—ammonium sulphate as basis for  
 acidimetry, 88  
 Prussian blue, determination of, 557  
 Koch. *See* Treadwell, 288  
 Kochs and Seyfert—Seger cones, fusion  
 temperatures of, 177  
 König, J.—effluents, determination of carbon  
 in, 830  
 Kohn, C. A.—copper sulphate, electrolysis of,  
 as basis for acidimetry, 89  
 and Brislee and Froyssell—iron, purity of  
 electrolytic, 108  
 • Kolb and Davidson—chlorates, analysis of, 513  
 Koninck, L. de. *See* De Koninck  
 Kratschmer—thiosulphate, sodium bromate for  
 standardising, 121  
 • Krauch—hydrochloric acid, examination of, 413  
 nitric acid, analysis of, 336  
 sodium carbonate, examination of, 460, 461,  
 462  
 sodium chloride, examination of, 403  
 Kraut—potassium tetroxalate as basis for  
 acidimetry, 92  
 Kreider—perchloric acid, preparation of, 523  
 Kreiling, P.—clays, determining the refractori-  
 ness of, 578  
 clays, rational analysis of, 586  
 Kretschmar—aluminium sulphate, analysis of,  
 610, 611  
 arsenic in hydrochloric acid, determination  
 of, 416  
 Kröhnke and Biltz—sewage and effluents,  
 determination of colloidal matter in, 814  
 Kühling—cyanamide, estimation of, 553  
 potassium tetroxalate as basis for acidimetry,  
 92  
 • Kühn, J.—soil, determining coarseness of, 844  
 Kühn—temperature measurement with ther-  
 mometers, 174  
 and Saeger—arsenic, modified Marsh test  
 for, 371  
 • Küster—indicators, theory of, 59  
 methyl orange, effect of carbonic acid on, 62  
 oxalic acid in volumetric analysis, 95  
 phenolphthalein in alkali determinations, 73  
 sodium hydroxide solutions, standard, from  
 sodium, 97  
 Küster and Grütters—barium hydroxide solu-  
 tions, standard, 97  
 methyl orange, end-point with, 57  
 and Münch—hydrochloric acid, preparation  
 of standard, 90  
 and Siedler—hydrochloric acid, preparation  
 of standard, 90  
 Kunkel—mercury vapour in air, estimation  
 of, 905  
 and Welzel—air, estimation of carbon mon-  
 oxide in, 893  
 • Kuppfer. *See* Dupré, 92  
 LANGE, A.—chlorine, liquid, properties of, 518  
 Langen—manometer, 169  
 Law. *See* Chapman, 371  
 Lean and Whatmough—iodine, pure, from  
 cuprous iodide, 120  
 Le Chatelier—chimney gases, testing, 191  
 pyrometer, optical, 177  
 thermo-electric, 181  
 Lecrenier—lead oxide, examination of, for  
 copper and iron, 629  
 Ledebur—iron, purity of electrolytic, 108  
 Lehmann—air, determination of sulphur di-  
 oxide in, 886  
 air, effect of the impurities in, 908  
 aniline in air, estimation of, 909  
 and Arens—dust in air, estimation of, 901  
 Lengfeld—permanganate determination, accu-  
 racy of the nitrometer method of, 112  
 Lestelle—sodium sulphide in black ash,  
 estimation of, 457  
 Letts and Blake—carbon dioxide in air, deter-  
 mination of, 872  
 Levot and Poggiale—manganese ore, estima-  
 tion of active oxygen in, 478  
 Leybold. *See* Moldenhauer, 560  
 Liebermann, C.—glass, alkaline reaction of, 54  
 Liebig—cyanides, analysis of, 547, 550  
 hydrocyanic acid, analysis of, 548  
 sodium carbonate solutions, influence of  
 temperature on specific gravity of, 449  
 Lindemann—oxygen in Glover tower exit gases,  
 apparatus for estimating, 335  
 Linder—thiocyanates, estimation of, 565  
 Lindo-Gladding—potassium, determination of,  
 526  
 Ling and Rendle—hydrochloric acid for the  
 Marsh test, purifying, 373  
 Lipp. *See* Schneider, 605  
 List—arsenic in pyrites, estimation of, 284  
 copper in pyrites, estimation of, 287, 298  
 sulphur in pyrites, estimation of, 276  
 • Loebell—cement, detection of adulteration of,  
 727  
 Logea, G.—soils, determination of humus in,  
 857  
 Lohöfer. *See* Lunge, 58, 74  
 Lowry. *See* Bousfield, 96, 463, 464  
 Lubberger—cyanogen compounds, estimation  
 of, 561  
 Luck—phenolphthalein as indicator, 71  
 Lüttke—litmus solution, preparation of, 68  
 Lunge—alkali hydroxides, titration with, 98  
 alumina, titration of, 66  
 aluminate of sodium, analysis of, 618

- Lunge—arsenious acid solution, preparation of, decimormal, 122  
 ash in fuel, determination of, 243  
 bleaching powder, analysis of, 504  
 burette stopcocks, greasing, when used with permanganate, 102  
 • burettes, reading, 49  
 carbon dioxide in sodium bicarbonate, estimation of, 470  
 chimney gases, loss of heat in, 238  
 chlorine and bromine, simultaneous estimation of, by iodometry, 116  
 chlorine and hypochlorous acid, distinguishing free, 510  
 dimethylaminoazobenzene as indicator, 67  
 drips from sulphuric acid chambers, examination of, 341  
 ferric salicylate as indicator, 77  
 gas analysis apparatus, modified Orsat, 201  
 gas-volumeter, 140, 145, 147  
 gas-volumeter, stand for, 154, 155  
 Gay-Lussac acid, examination of, 343  
 glass, decomposition of, by alkali carbonate, 54  
 hydrochloric acid, determination of sulphuric acid in, 414  
 iodic acid, behaviour of, with methyl orange, 93  
 iodine solutions, action of, on rubber, 113  
 iodine solution, preparation of pure, 119  
 iodine solutions, standardising, by sodium sulphite, 115  
 iron, purity of electrolytic, 108  
 iron in sulphuric acid, determination of, 381  
 kiln gases, determination of total acidity of, 299, 302, 304  
 litmus and methyl orange, comparative sensitiveness of, 69  
 manganese ore, estimation of active oxygen in, 479  
 methyl orange as indicator, 61  
 nitrates in saltpetre, determination of, by the nitrometer, 315  
 nitrate oxide in chamber exit gases, detection of, 339  
 nitrometer, 132  
   device for avoiding loss of nitrous fumes in the, 136  
   *o*- and *p*-nitrophenol as indicators, 77  
 • nitrous acid in sulphuric acid, detection of, 361  
   nitrous acid, titration of, 66  
   nitrous oxide in chamber exit gases, determination of, 340  
   oxalic acid, testing purity of, 104  
   oxalic acid in volumetric analysis, 95  
   permanganate, nitrometer method of standardising, 109  
   permanganate solutions, stability of, 101  
   phenolphthalein for alkali determination, 73  
 • pipettes, delivery of, 42  
 • potassium tetroxalate as basis for acidimetry, 92  
 • sodium arsenite and thio sulphate in iodimetry, 123
- Lunge—sodium bicarbonate as basis for acidimetry, 90  
 • sodium carbonate, preparation of, as basis for acidimetry, 84, 85  
 sulphur in pyrites, determination of, 272, 295  
 • sulphuric acid, specific gravity of, 347, 350, 354  
   water for boilers, etc., examination of, 806  
   water, determination of alkalinity of, 738  
   and Bachofen—bleaching powder, strengths of, 499, 500  
 and Hurter—methods of sampling, 8  
 and v. Keler—aluminium sulphate, analysis of, 608  
 and Lohüfer—sodium salts, titrating certain, with phenolphthalein, 58  
   sodium silicate, titration of, 74  
 and Lwoff—nitrous and nitric acids in sulphuric acid, determination of, 377, 379  
 and Marchlewski—carbon dioxide, determination of, 149  
   hydrochloric acid solutions, specific gravity of, 412  
 and Millberg—alkali hydroxides, action of, on glass, 95  
   clay, rational analysis of, 585  
   puzziolanas, 675  
 and Rey—nitric acid, specific gravity of, 323, 324  
   weighing apparatus for fuming acids, etc., 390  
 and Rittener—carbon dioxide, determination of, 153  
   carbon dioxide in presence of chlorine, determination of, 515  
   carbon dioxide in presence of hydrogen sulphide, determination of, 439  
   chlorine in Deacon gases, determination of, 494  
 and Schläppi—sodium ferrocyanide in "vat liquor," estimation of, 427  
 and Schochor-Tscherny—marls, examination of, 683  
 and J. H. Smith—sulphur compounds in soda mother liquors, estimation of, 433  
 and Stierlin—sulphur in blende, determination of, 298  
 and Zeckendorf—carbon dioxide in air, approximate estimation of, 875  
   *See* Harbeck, 898  
 Lux—manometer, modified Langen's, 169  
 Lwoff. *See* Lunge, 377, 379
- MACAGNO—sulphur, determination of, in native sulphur, 468  
 M'Cay—arsenic in pyrites, estimation of, 282  
 Macfarlane and Caldwell—gas analysis apparatus, 219  
 Märcher, M.—spoils, determination of phosphoric acid in, 855  
 Mahler—bomb, 256  
 • Mann, C.—thiocyanates from chlorides, separation of, 565  
 • Mann. *See* Erdmenger, 699

- Marbontin and Moulinié—sulphuric acid, estimation of, 279
- Marchlewski. *See* Lunge, 149, 412
- Marcilli—sulphur, determination of, in native sulphur, 268
- Marsh—arsenic test, 363
- Marshall, A.—sulphuric acid, standard, 90
- Marx and Trommsdorff—nitric acid in water, determination of, 754
- Maynard—lime, analysis of, 483
- Meade—sulphuric acid, preparation of standard, by electrolysis of copper sulphate, 90
- Meineke—iodine, preparation of pure, 120
- iron alum for standardising permanganate, 109
- potassium bi-iodate as basis for acidimetry, 89, 93
- potassium tetroxalate as basis for acidimetry, 92, 105
- sodium thiosulphate, purification of, 117
- thiosulphate, potassium chromate for standardising, 121
- Meissl. *See* Ulbricht, 92
- Mennicke—chlorate, perchlorate, and chloride, estimation of, in mixtures, 322
- Messner—lactmoid as indicator in titrating cinchona alkaloids, 76
- Metz—iodine solutions, standardising, by tartar emetic, 115
- Meyer, F.—zinc in blende, estimation of, 291
- Meyer, F. M.—Portland cement, volumeter for, 700
- Meyer, V., and Riddle—pyrometer, air, 175
- Meyer—generator gas, apparatus for the analysis of, 205
- Michaëlis—cement, apparatus for examining the permeability of, 712
- cement briquettes, apparatus for removing, from moulds, 720
- cement, determination of alkalis in, 694
- cements, apparatus for measuring the tensile strain of, 721
- mortar-volumenometer, 670
- volumenometer, 590
- Milbauer—cyanates, determination of, 553
- Millberg. *See* Lunge, 95, 585, 675
- Miller—ammonia in water, determination of, 768
- tropæolin OO as indicator, 76
- Mohr, F.—oxalic acid as basis for alkalimetry, 83
- silver nitrate in volumetric analysis, 123
- Mohr—acidimetry, iodometric method of, 89
- calcium in water, determination of, 764
- ferrous ammonium sulphate for standardising permanganate, 108
- unit of volume (Mohr's litre), 34
- Mohr-Clasen—litmus, extraction of, 67
- Moldenbauer and Leybold—Prussian blue, analysis of, 560
- Moody, G. T.—hydrochloric acid solution, preparation of normal, 90
- Moody, S. B.—aluminium sulphate, determination of free acid in, 614
- Morse and Chambers—hydrogen peroxide, use of, as basis for acidimetry, 89
- Morse and Chambers—permanganate solution, standardisation of, 109
- Motion. *See* Worden, 91
- Moulinié. *See* Marbontin, 279
- Müller, F. C. G.—sampling effluents, 809
- water, apparatus for estimating dissolved gases in, 827
- Müller, G.—hydrometer, differential, 163
- Müller, M.—glass, estimation of alkali in, 649
- Müller, W. A.—sulphuric acid, determination of, 280
- Münch. *See* Kuster, 90
- Müncke—gas burner, 29
- Murmann—zinc in blende, estimation of, 292
- Mutnicksky—barium thiosulphate solution, normal, 122
- starch solution, preservation of, 114
- Mylius—glass, action of water, acids, etc., on, 636, 640
- and Förster—iodo-cosine as indicator, 76
- See* Förster, 641
- NAEF—sulphuric acid solutions, specific gravity of, 347, 350
- Nahnsen—copper in pyrites, estimation of, 286
- National Physical Laboratory—standardisation of vessels, 33, 36, 41
- Naumann. *See* Goldberg, 77
- Nauss—Prussian blue, determination of, 558
- Neher—arsenic in sulphuric acid, determination of, 384
- Neitzel—sodium as basis for acidimetry, 88
- Neppi. *See* Barbieri, 105
- Nessler, J.—ammonia in water, determination of, 765
- Neubauer—potassium, determination of, 527
- Newbury—calcium and magnesium, volumetric determination of, 663
- Nieloux—carbon monoxide in air, estimation of, 895
- Nikaido—sulphuric acid, determination of, 279
- Nobel—sand in clay, apparatus for estimating, 690
- Noll, H.—sewage, determination of oxidisability of, 815
- North and Blakey—sodium bicarbonate as basis for acidimetry, 90
- sodium carbonate, preparation of pure, 85
- Nourisson—chlorine, examination of electrolytic, 495
- ODDY and J. B. Cohen—permanganate solutions, stability of, 101
- Orsat—gas analysis apparatus, 198
- Ostwald—indicators, theory of, 59
- pipette, 42
- pipettes, delivery of, 41
- Otto—arsenic in hydrochloric acid, test for, 415
- PARNELL—"vat liquor," estimation of silica, alumina, and iron in, 428
- Parr—calorimeter, 256
- Passon—limestone, analysis of, 482
- Peake. *See* Warrington, 858
- Péclet—velocity of gas current, calculation of, from manometer readings, 169
- Penot—bleaching powder, analysis of, 503

- Perman and John—borax as basis for acidimetry, 88  
 Perrot—gas oven, 30  
 Petersen—acid in coloured extracts, beer, etc., determination of, 89  
 Petriccioli. *See* Reuter, 122  
 Pettenkofer—carbon dioxide in air, determination of, 870  
 Pettersson—carbon dioxide, determination of, 149  
 Pfeifer—magnesium in water, determination of, 764  
 Pfeiffer, O.—pyrometers, modification of thermometer, 183  
     sulphur in gas residuals, determination of, 271  
 Philipp. *See* Fischer, B., 67  
 Pillitz, W., and N. Zalomanoff—soils, determining absorptive power of, for salts, 850  
 Pincus—calc spar as basis for acidimetry, 88  
 Plimpton and Chorley—barium thiosulphate for iodimetry, 122  
 Poggiale. *See* Levoll, 478  
 Pohl—nitrous oxide in gases, determination of, 340  
 Pontag—carbon monoxide in air, estimation of, 894  
     tobacco smoke, 910  
 Pontius—bleaching-powder, analysis of, 503  
 Poppenberg. *See* Wohl, 148  
 Precht—magnesium in potash salts, determination of, 531  
     *See* Röttger, 534  
 Preusse. *See* Tiemann, 759  
 Prinsep—temperature measurement by observing fusion of alloys, 176  
 Prost and Balthaser—fluorine in zinc blende, determination of, 293  
  
**QUINCKE**—acidimetry, standardising solutions for, 91  
  
**RAOULT**—gas burette, 195  
 Raschig—alkali hydroxides, titration with, 98  
     hydrochloric acid solutions, preparation of standard, 90  
     iodine and sulphurous acid, reaction between, 116  
     sulphuric acid, estimation of, by benzidine, 280, 281  
 Rasenack—potassium chlorate, analysis of, 498  
 Reed—selenium in sulphur, determination of, 268  
 Reich—sulphur dioxide in kiln gases, determination of, 300  
 Reinhardt—permanganate, titration of iron solutions with, 109  
 Reinitzer—ammonium chloride as basis for acidimetry, 88  
     litmus as indicator, 68, 69, 70  
 Reinsch—arsenic, test for, 374  
 Reuter and Petriccioli—arsenious acid solution, preparation of decipormal, 122  
 Rey—float for burettes, 48  
     *See* Lunge, 323, 324, 390  
 Richardson and Aykroyd—sulphate in soda mother liquors, estimation of, 434  
 Richmond—borax as basis for acidimetry, 88  
 Richter—potassium bichromate as basis for acidimetry, 93  
 Riddle. *See* Meyer, V., 175  
 Riegler—iodic acid as basis for acidimetry, 89  
     nitrous acid, determination of, 343  
     nitrous acid in sulphuric acid, detection of, 361  
     oxalic acid solution, preparation of, 104  
     sulphuric acid, determination of, 279  
 Rimbach and Worms—borax as basis for acidimetry, 88  
 Rittener. *See* Lunge, 153, 439, 494, 514  
 Robert and Roncali—hypochlorites, determination of, 509  
 Rössler—gas oven, 30  
 Röttger and Precht—sodium in potassium chloride, determination of, 534  
 Rolland. *See* Schlösing, 198  
 Roloff—indicators, theory of, 59  
 Roncali. *See* Robert, 509  
 Rose—potassium, determination of, 524  
 Rosenblatt—boric acid, estimation of, 653  
     glass, detection of boric acid in, 643  
 Rosenfeld and Silber—rubrescin as indicator, 76  
 Rosenlecher—sulphuric acid and anhydride, analysis of, 392  
 Roth—hydrochloric acid solutions, preparation of standard, 90  
 Ruber—specific gravity, determination of, 163  
 Rübner—mercaptan in air, detection of, 906  
     soot in air, determination of, 901  
 Rudolf—drying precipitates on filter papers, 28  
 Rürup—hydrochloric acid, determination of sulphuric acid in, 414  
 Rüst—manganese oxalate for standardising permanganate, 105  
 Rupp—sulphur dioxide solutions, titration of, with iodine, 116  
  
**SABECK**—clays, analysis of, 585, 587  
 Salm—indicators, sensitiveness of, 78  
 Salomon, F.—barothermoscope, 148  
 Salzer—borax as basis for acidimetry, 88  
 Sand and Hackford—arsenic, electrolytic determination of, 371  
 Sanger, C. R., and O. F. Black—arsenic, estimation of, by the Gutzeit test, 376  
 Sauer, E. *See* Weber, R., 636, 640  
 Schaak, M.—boric acid, estimation of, 626  
 Scheibler and Dietrich—calcium carbonate in limestone, apparatus for determining, 659  
 Schläppli—arsenic, determination of, in sulphur, 267  
     *See* Lunge, 427  
 Schlaud—cyanogen, estimation of, 551  
 Schlickum—arsenic in hydrochloric acid, detection of, 415  
 Schlösing—nitrate in saltpetre, determination of, 317  
     soils, analysis of, 847  
     and Rolland—gas analysis apparatus, 198  
 Schloesser—expansion of glass, corrections for, 36, 37, 38, 46  
     pipettes, delivery of, 42  
     standardising apparatus, 33  
  
     3 R



- Schloetter—chlorine, estimation of, in Deacon gases, 495
- Schmatolla—titration with phenolphthalein in alkaline solution, 474
- Schmidt, W.—burette for titrating several solutions, 52
- Schmitz-Dumont—carbon disulphide in air, estimation of, 906
- Schneider and Lipp—bauxite, analysis of, 605
- Schoch—cement analysis, 692, 693  
lime, slaking power of, 669
- Schochor-Tscherny. *See* Lunge, 683
- Schöne—hydrogen peroxide in air, 879  
sand in clay, apparatus for estimating, 69
- Scholtz—chlorates, determination of, 513
- Scholvien—potassium chlorate, detection of nitrate in, 518
- Schondorff—coke from various coals, characteristics of, 245
- Schranz. *See* Dohrner, 393
- Schultze—expansion of liquids, corrections for, 45
- Schulze and Tiemann—effluents, determination of nitrates in, 822  
nitric acid in water, determination of, 753
- Schumann—volumeter for cement, 698
- Sebelien—sodium carbonate, purification of, 85
- Seger—clays, determining refractoriness of, 577  
clays, rational analysis of, 586  
cones, fusible, 176  
differential manometer, 167  
gas oven, 30
- Seger, H., and E. Cramer—claywares, determining stability of, towards acids, 602
- Selckmann—perchlorate in Chili saltpetre, determination of, 320
- Sell—water, determination of residue on evaporating, 737
- Seybel and Wikander—arsenic, test for, 376
- Seyda and Weinig—ammonium chloride as basis for acidimetry, 88
- Seyfert. *See* Kochs, 177
- Shearer. *See* Giles, 305
- Seidler. *See* Küster, 90
- Sievert—nitrate in saltpetre, estimation of, 310
- Silber. *See* Rosenfeld, 76
- Silberberger—sulphuric acid, precipitation of, by strontium chloride, 277
- Siemens—pyrometer, electric resistance, 179
- Simmons and Abady—combustion recorder for chimney gas analysis, 191
- Skrabal—iron in sulphuric acid, determination of, 380  
permanganate, standardising, by iron, 106, 107
- Smith, J. H. *See* Lunge, 433
- Smith, J. L.—glass, determination of alkali in, 649
- Soden, W. H.—gas analysis apparatus, modified Orsat, 203  
gas analysis apparatus, 219  
gas analysis, sampler for, 193
- Sörensen—sodium carbonate, purification of, 85  
sodium oxalate as basis for acidimetry, 85, 86  
sodium oxalate for standardising permanganate, 103
- Spiegel—*p*-nitrophenol as indicator, 77
- Spitta—carbon monoxide in air, estimation of, 896
- Spitz. *See* Hönig, 654
- Spüller. *See* Kälmann, 431
- Stanger and Blount—cement analysis, 693
- Stead—gas sampler, 193
- Steinbrück-Schmelzer—cement, apparatus for preparing test-pieces of, 716
- Stephens. *See* Symons, 872
- Stieglitz—indicators, theory of, 59
- Stierlin. *See* Lunge, 268
- Strache, Johoda, and Genzken—"Autolysator," 191
- Strobel—filter papers, increase in weight of, on drying, 23
- Stutzer—barium hydroxide solution, standard, 99  
nitrate in saltpetre, determination of, 309
- Sundström—sodium bicarbonate, analysis of, 469
- Symons and Stephens—carbon dioxide in air, estimation of, 872
- Syniewski—starch, preparation of soluble, 744
- TAUREL—bauxite, analysis of, 607
- Teclu—gas burner, 30
- Telle—sulphuric acid, determination of, 379
- Teimajer—cement briquettes, rammer for moulding, 719  
cement, permanency of volume of, 710
- Thiele and Richter—calc spar as basis for acidimetry, 88
- Thompson, L.—calorimeter, 360
- Thomson, R. T.—Congo red as indicator, 77  
dimethylaminobenzene as indicator, 67  
indicators, basicity of acids towards, 74, 75  
methyl orange, 61  
sodium silicate, titration of, 74  
sulphurous acid, titration of, using litmus as indicator, 65
- Thomson, W.—arsenic, electrolytic determination of, 371  
calorimeter, 362
- Tiemann and Preusse—nitrous acid in water, determination of, 759  
*See* Schulze, 753, 822
- Topf—thiosulphate solutions, preparation of, 121
- Traub and Hock—lactol as indicator, 75
- Treadwell—carbon dioxide in chlorine, burette for estimating, 492  
drying cupboard, 29  
iodine solutions, action of dilute, with starch, 113  
iodine solutions, preparation of pure, 119  
iron, electrolytic, for standardising permanganate, 107  
permanganate solutions, stability of, for potassium bi-iodate, purity of, 120  
thiosulphate solutions, preparation of, 121  
titrations with methyl orange, 63  
and Christie—chlorine in gases, estimation of, 493, 494  
and Koch—carbon in pyrites, estimation of, 288
- Trillich—water, determination of free carbonic acid in, 762

- Troeger and Hille—diaminoazotoluene-sulphonic acid as indicator, 76  
 Trotman—arsenic, Marsh-Berzelius test for, 371  
 TUNNICLIFFE and Meissl—potassium tetroxalate as basis for acidimetry, 92  
 Ullrich—nitrate in saltpetre, determination of, 310, 311  
 nitric acid in water, determination of, 753  
 VAN BREUKELERVEN—perchlorate in sodium nitrate, detection of, 307  
 Vanino—bleaching powder, analysis of, 506, 507  
 chlorine, weight of 1 c.c. of, 507, 508  
 permanganate determination, accuracy of methods of, 112  
 Veley and Manley—nitric acid, specific gravity of, 324  
 Venable—hydrochloric acid, detection of iron in, 316  
 Vetsch, *See* Fritsch, 23  
*See* Isbert, 408  
 Verwer and Groll—iron, purity of electrolytic, 108  
 Vignon and Meunier—water for boilers, etc., examination of, 802  
 Ville, *See* Engel, 28  
 Vogel and Hälcke—potassium, determination of, 525  
 Vohl, H.—effluents, detection of coal-gas products in, 833  
 Volhard—chlorides, estimation of, in presence of thiocyanates, 566  
 iodine and sulphurous acid, reaction between, 115  
 permanganate, iodometric determination of, 109  
 thiocyanate solution, standardising, by silver nitrate, 129  
 thiocyanates, estimation of, 566  
 Vollers—crucible, improved Gooch, 26  
 Von Jüptner—carbon in fuel, determination of fixed, 144  
 Von Kéler, *See* Lunge, 608  
 Von Knorre—nitric oxide in chamber exit gases, determination of, 339  
 Von Than—potassium bi-iodate as basis for acidimetry, 89  
 WADDELL—indicators, theory of, 59  
 Wages, J.—indicators, classification of, 56  
 indicators, theory of, 59  
 liquids, wetting of glass by, 50  
 potassium bi-iodate as basis for acidimetry, 93  
 potassium tetroxalate as basis for acidimetry, 92  
 Wagner—azotometer, 132  
 burettes, time of delivery of, 41  
 nitrogen determination by the azotometer, 136, 137  
 standardising apparatus, 33  
 thiosulphate, potassium bichromate for standardising, 121  
 weighing in air, correction for, 21  
 Wahnschaffe, F.—soils, determination of sulphur in, 863  
 soils, examination of, 841  
 Walker—iodic acid for standardising thiosulphate, 121  
 Walland—saltcake, determination of calcium in, 406  
 Wanner—optical pyrometer, 177  
 Ward, *See* Frankland, 215  
 Warder—alkali in normal carbonates, estimation of, 73  
 Warington and Peake—soils, determination of carbon in, 858  
 Watson—soda vat waste, analysis of, 436  
 sulphur in iron pyrites, estimation of, 295  
 Wdowiszewski—ferric oxide for standardising permanganate, 109  
 Weber, R., and E. Sauer—glass, action of water, acids, etc., on, 636  
 glass, examination of resistance of, 640  
 Weber—cement, apparatus for measuring crushing strain of, 725  
 Wedgwood—pyrometer, 176  
 Weinhold—thermometer block for temperature measurement, 174  
 Weinig, *See* Seyda, 88  
 Weldon—chlorine manufacture, examination of liquors in, 485  
 Wells—potassium tetroxalate as basis for acidimetry, 92  
 Welzel, *See* Kunkel, 893  
 Whatmough, *See* Lean, 120  
 Wheeler, R. V., *See* Bone, W. A., 219  
 White, A. H.—aluminium sulphate, determination of free acid in, 616  
 Wiborg—thermophone, 177  
 Wiernik, J. and S.—magnesium chloride in sodium chloride, determination of, 402  
 Wiesnegg—gas burner, multiple flame, 30  
 Wikander, *See* Seybel, 376  
 Wild, *See* Engler, 881  
 Wildenstein—sulphuric acid, determination of, 278  
 Wilsing—sulphuric acid, determination of, 278  
 Windaus, *See* Autenrieth, 432  
 Winkler, C.—burettes, reading, 44  
 carbonates, titration of, using phenolphthalein, 72  
 carbon monoxide, absorption of, by cuprous chloride, 210  
 explosion pipette, 214  
 gas burette, 194  
 nitrous oxide in chamber exit gases, determination of, 340  
 oxalic acid, preparation of pure, 91  
 oxygen in Glover tower exit gases, apparatus for estimating, 335  
 sulphuric acid, weighing apparatus for, 389  
 Winkler, L. W.—absorption coefficients in water of oxygen, nitrogen, hydrogen, and carbon monoxide, 225  
 water analysis, 742, 743, 750, 762, 767, 773, 777, 787  
 water, determination of dissolved oxygen in, 782  
 water, dissolved gases in, 785, 786

- Winteler—perchlorate in Chili saltpetre, determination of, 320
- White—pyrometer, air, 175
- Wohl, A.—volume of gases, apparatus for measuring, 148
- Wolff, J.—ferric salicylate as indicator, 77
- Wolff, E.—soils, determination of ammonia in, 861
- Wolff, J.—boric acid, analysis of, 626
- Wolpert, H.—carbon dioxide in air, estimation of, 876
- Worden and Motion—sulphuric and hydrochloric acids, specific gravities of solutions of, 91
- Worms. *See* Rimbach, 88
- Wroblewsky—starch, preparation of soluble, 121
- YOUNG, S. W.—iodine solutions, standardising, by thiosulphate, 125
- Younger—chlorine in the Deacon process, estimation of, 488, 489
- YALOMANOFF, N.—*See* Pollitz, 850
- Zaboriecki—ferrocyanide in "cat liquor," estimation of, 428
- Zeckendorf. *See* Lunge, 875
- Zimmermann—permanganate and hydrochloric acid, interaction of, 102
- Zschimmer—boric acid, examination of, 624
- Zulkowski—ferrocyanide in "cat liquor," estimation of, 428
- Prussian blue, determination of, 568
- thiosulphate, potassium chromate for standardising, 121

In active preparation.

# TECHNICAL METHODS OF CHEMICAL ANALYSIS

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IN COLLABORATION WITH OTHER EXPERTS

## ENGLISH TRANSLATION

FROM THE LATEST GERMAN EDITION, ADAPTED TO ENGLISH  
CONDITIONS OF MANUFACTURE

EDITED BY

CHARLES ALEXANDER KEANE, D.Sc., Ph.D.

PRINCIPAL AND HEAD OF THE CHEMISTRY DEPARTMENT  
THE SIR JOHN CASS TECHNICAL INSTITUTE, LONDON

IN COLLABORATION WITH OTHER EXPERTS

VOLUMES II. AND III.

GURNEY AND JACKSON

10 PATERNOSTER ROW, LONDON

1908

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